

"PATENT"

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of
Noyes L. Avery et al

U. S. Serial No. 09/967,265

Filed: August 28, 2001

A Method for Controlling Deposit Formation
in Gasoline Direct Injection Engine by Use
of a Fuel Having Particular Compositional
Characteristics

) Before the Examiner
) Margaret B. Medley
)
)
) Confirmation Number: 5218
)
) Group Art Unit: 1714
)
) Family Number: P2000J093-US2
)
)

Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

Sir:

COPIES OF ITEMS REFERENCED IN ACCOMPANYING
DECLARATION UNDER 37 CFR 1.132

Applicants take this opportunity to submit to the Examiner copies of three SAE papers which are referenced in the accompanying Declaration under 37 CFR 1.132. These SAE papers compare gasoline direct injector systems against port fuel injector

CERTIFICATION OF FACSIMILE TRANSMISSION		
I hereby certify that this paper is being facsimile transmitted to the Commissioner for Patents facsimile number 1-703-872-9311 on the date shown below.		
<u>Susan Fleming</u>	<u>Susan Fleming</u>	<u>8/12/03</u>
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systems, discuss the suppression of deposits on fuel injectors for direct injection gasoline engines and study combustion chamber deposits and the influence of fuel component and gasoline detergent in combustion chamber deposits. They are offered as background and support for the present invention.

"A Comparison of Gasoline Direct Injection Part 1 - Fuel System Deposits and Vehicle Performance," Arters, Bardasz, Schiferl and Fisher, SAE 1999-01-1498.

"A Method for Suppressing Formation of Deposits on Fuel Injector For Direct Injection Gasoline Engine," Kenoshita, Saito, Matsushita, Shibata and Neiwa, SAE 1999-01-3656.

"Study on Combustion Chamber Deposit Formation Mechanism - Influence of Fuel Components and Gasoline Detergents," Uehara, Takei, Hoshi, Shiratani, Okada, Esaki, SAE 971722.

Respectfully submitted,



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☒ Pursuant to 37 CFR 1.34(a)

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8/8/03

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)	Group Art Unit: 1714
A METHOD FOR CONTROLLING DEPOSIT)	
FORMATION IN GASOLINE DIRECT)	Family Number: P2000J093-US2
INJECTION ENGINE BY USE OF A FUEL)	
HAVING PARTICULAR COMPOSITIONAL)	
CHARACTERISTICS)	

Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

Sir:

DECLARATION UNDER 37 CFR 1.132

Noyes L. Avery declares:

That: I am a joint inventor of the subject matter of the present application;

That: I have read and am familiar with the teachings of USP 6,187,171 to Tsuboi;

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That: I understand the invention of Tsuboi to be an unleaded high octane gasoline fuel composition comprising (A) at least one reformat fraction produced by a continuous regeneration type reformer and/or (B) at least one reformat fraction produced by a fixed-bed type reformer, said unleaded, high octane gasoline composition satisfying the following conditions (1), (2) and (3).

(1)

$$Z = (1/100 [\Sigma(ax) + (1/9) \Sigma(by)]) < 0.010$$

wherein, $\Sigma(ax)$ is a summation of (ax), wherein (a) is content (vol%) by volume of a fraction falling into the reformat fraction A, (x) is content (vol%) by volume of aromatic hydrocarbons having a carbon number of 11 or more in the fraction (a), and $\Sigma(by)$ is a summation of (by), wherein (b) is content (vol%) by volume of a fraction falling into the reformat fraction (B), (y) is content (vol%) by volume of aromatic hydrocarbons having a carbon number of 11 or more in the fraction (b),

(2) content of aromatic hydrocarbons having a carbon number of 7 to 8 being 30 vol% or more, and

(3) research octane number being 96.0 or more;

That: I understand from the Tsuboi text that the combustion of such a fuel in a gasoline spark ignition engine results in a reduction of combustion chamber deposits and intake valve deposits;

That: comparative Examples 1 and 2 of Tsuboi employ a mixture of 17% and 25%, respectively, of Reformat A, containing 0.35 vol% of C11⁺ aromatic

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hydrocarbons, 50% and 45%, respectively, of FCC naphtha which is a light naphtha, 17% and 15%, respectively, of Reformate B containing zero C11⁺ aromatic hydrocarbons, 12% and 11%, respectively, of alkylate and 4% each of butane, and that these comparative fuels were characterized by Tsuboi as exhibiting 198 and 170 mg/valve IVD and 1.14 and 148 g/cylinder CCD, respectively;

That: from Tsuboi this data was taken as showing that such fuels, when compared against the fuel of Tsuboi's invention, were inferior in the reduction of CCD and IVD;

That: the fuels exemplified in the present application in Table 3 (Fuels Aro-1, Aro-2 and Aro-3) all used 98 RON Reformate which was a fixed bed reformat and contained 3.32% C11⁺ aromatics (as a part of the whole reformat);

That: using Tsuboi's formula, the Aro-1, Aro-2 and Aro-3 fuels possessed the following z factors:

$$\begin{aligned}\text{Aro-1/Aro-3} \quad z &= 1/100 [\Sigma(ax) + 1/9 \Sigma(by)] \\ z &= 1/100 [O + 1/9 (15 \times 3.32)] \\ z &= 0.0553\end{aligned}$$

$$\begin{aligned}\text{Aro-2} \quad z &= 1/100 [\Sigma(ax) + 1/9 \Sigma(by)] \\ z &= 1/100 [O + 1/9 (55 \times 3.32)] \\ z &= 0.202\end{aligned}$$

That: based on this it is apparent that the information contained in the present application is based on examples corresponding, at best, to Tsuboi's comparative examples which were presented by Tsuboi as demonstrating fuels

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which were not as effective at reducing IVD and CCD as was the fuel corresponding to Tsuboi's invention;

That: in so far as the examples of the present application correspond more closely to the comparative examples of Tsuboi rather than the invention example of Tsuboi, it is not at all apparent that GDI deposits could be controlled or reduced by combusting a fuel containing aromatics attributable to reformates in general, light FCC fractions, or mixtures of reformates in general with light FCC fractions;

That: in GDI engines, IVD is phenomenon associated with the oil and not with the fuel whereas in port fuel injection engines, IVD is associated with the fuel, see SAE Paper 1999-01-1498 "A Comparison of Gasoline Direct Injection Part 1 - Fuel System Deposits and Vehicle Performance," Arters, Bardasz, Schiferl and Fisher at page 996 "Intake Valve Deposits."

That: in SAE paper 1999-01-3656 "A Method for Suppressing Formation of Deposits on Fuel Injector for Direct Injection Gasoline Engine" Kinoshita, Saito, Matsushita, Shibata, Niwa, it is speculated that, based on functional group analyses, injection deposits were mainly constituted of functional groups with abundant oxygen which composition was similar to that of the deposits in the combustion chambers of gasoline engines (pg. 2178);

That: in that SAE paper [1999-01-3656] at page. 2179 it is stated that in light of correlation coefficients, the fuel flow rate change through the injectors due to deposit accumulation was related to the distillation characteristic of the fuel while the correlation coefficient for the aromatic content was very low;

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That: according to that paper it was observed that the flow rate change in direct injectors was restrained when the nozzle temperature was lower than the 90 vol% distillation temperature of the fuel, (the T₉₀ of the fuel);

That: in SAE 971722 "Study on Combustion Chamber Deposit Formation Mechanism - Influence of Fuel Components and Gasoline Detergents" Uehara et al., it is stated that the formation of CCD is known to increase with increased aromatics or heavy fraction components in gasoline, that aromatic compounds in fuels have a strong tendency to promote formation of CCD and that the tri- and tetra-substituted benzenes tend to produce more CCD than do the di-substituted benzenes which themselves produce more CCD than do toluene or benzene per se;


That: based on this it is not apparent that with respect to fuels which have similar T₉₀ distillation temperatures (see Aro-1, Aro-2 and Aro-3 fuels in Table 3 of the present application) that fuels (Aro-2 and -3) which have the highest concentration of aromatics per se as well as the greatest amount of aromatics attributable to reformat in general and light FCC would have the effect of causing lower GDI injector tip deposit formation as compared against fuels of lower aromatic content and different source (Aro-1); and this is especially true in view of the fact that Aro-1 and Aro-2 and Aro-3 all apparently correspond to the "comparative" fuels of Tsuboi which were shown by Tsuboi to be inferior in reducing CCD and IVD as compared against the inventive fuel of Tsuboi's;

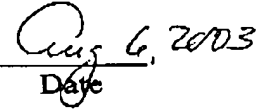
That: all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further,

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that these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001, Title 18 of the United States code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.


NOYES L. AVERY


Date

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1999-01-1498

A Comparison of Gasoline Direct Injection Part I – Fuel System Deposits and Vehicle Performance

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ABSTRACT

Four 1998 Mitsubishi Carismas, two equipped with direct injection and two with port fuel injection engines, were tested in 20,100 km intervals to determine the effect of mileage accumulation cycle, engine type, fuel and lubricant on vehicle deposits and emissions, acceleration and driveability performance. The program showed that engine fuel system deposits, including specifically those on intake valves, combustion chambers and injectors are formed in higher amounts in the GDI engine than the PFI engine. The fuel additive used reduced injector deposits and combustion chamber deposits in the GDI, but had no significant effect on intake valve deposits, which are affected by crankcase oil formulation. In GDI vehicles, deposited engines were found to have increased hydrocarbon and carbon monoxide emissions and poorer fuel economy and acceleration, but lower particulate emissions. Effects in PFI engines were directionally the same for NOx and particulates but the opposite for HC and CO emissions and fuel economy. In terms of specific deposit effects in the GDI engine, CCD is correlated with poorer acceleration, HC and CO emissions, while injector deposits correlate with NOx formation.

INTRODUCTION

Direct injection gasoline engine technology has recently burst upon the automotive scene in concrete form with the commercial introduction by two different manufacturers. Mitsubishi currently offers vehicles equipped with their GDI[®] technology (1) in Japan and Europe, and Toyota offers their D4 direct injection technology (2) in Japan. Numerous other automakers have presented their own developments in the area of direct injection engines (e.g. 3, 4, 5).

Direct injection gasoline has long been of interest due to the potential for higher specific power and lower fuel consumption compared to conventional fuel delivery systems. The ability to produce a commercially viable

system meeting today's vehicle requirements is largely the result of advances in low cost electronically controlled fuel injection systems and developments in catalyst emission reduction systems. Still, the technology is in its infancy in the broad sense of consumer use and the specter of potential performance issues in the field warrant study on the road. In fact, concerns over reported field problems in Europe has led to the formation of CEC Technical Committee IF-034 to investigate potential pitfalls and solutions for direct injection gasoline technology.

The effect of intake system and engine deposits which accumulate over time on direct injection technology in terms of vehicle performance such as acceleration, emissions and driveability has not previously been discussed in the literature. In theory, injector deposit effects would have the same end result in GDI as PFI engines: poor atomization and targeting of the fuel leading to improper air-to-fuel (A/F) ratio. The primary mechanism of intake valve deposit (IVD) effects in PFI engines is of absorbing desorbing fuel into the deposit, creating a transient A/F disruption in the cylinder. In the case of GDI, where fuel is injected into the intake manifold, a performance effect would be expected only if IVD were sufficient large to decrease the amount of air flow into the cylinder. Combustion chamber deposits (CCD) should have the same insulating effect in GDI engines as PFIs, potentially leading to octane requirement increase and increase NOx emissions. GDI CCD also has the added potential of absorbing fuel as it is directly sprayed at the piston crown bowl or possibly disrupting the air flow critical to the stratified mixing. This could lead to poor A/F control in the spark plug region, resulting in misfire or knock. In general, little has been published on the response of this new engine technology to fuel and lubricant chemistry changes compared to conventional port fuel injection (PFI) technology.

The subject of this paper is a vehicle fleet trial undertaken to provide some of this information. The objective of this trial was to compare the fuel and lubricant performance requirements of matched pairs of Mitsubishi Ca

isma PFI and GDI% vehicles over cycles emphasizing the severity of lean burn and near stoichiometric (rich) operations. Performance was measured via deposit and wear evaluations, vehicle emissions (including particulates), fuel economy, acceleration and driveability.

Initial results related to engine deposits and engine oil performance have been presented (6). This paper includes subsequent data, which gives us a clearer picture of the effect of fuel additive and lubricant on engine deposits, and presents the effects of the deposits on vehicle performance. A companion paper, SAE 1999-01-1499, presents an in depth look at the crankcase oil performance in the fleet.

PROCEDURES

Four 1998 Mitsubishi Carismas, two equipped with direct injection and two with port fuel injection engines, were tested in 20,100 km intervals to determine the effect of mileage accumulation cycle, engine type, fuel and lubricant on engine deposits and oil performance parameters. Emissions, acceleration and driveability were measured at the beginning and end of each test to provide information on the effect of deposits. As part of a fractionated factorial statistical design, two levels each of cycle, fuel and crankcase oil lubricant were evaluated along with an assessment of car-to-car variation. Descriptions of the Vehicles, Fuel and Crankcase Lubricants are common between this paper and the companion paper. Detailed explanations of the Drive Cycles, Vehicle Preparation and Data Acquisition are presented here and summarized in the companion paper. Conversely, a summary of the Experimental Design is presented here with a detailed explanation in the companion paper. The description of the Deposit Measurements and Performance Tests are presented only in this paper, while descriptions of Engine Wear Measurements and Drain Oil Analysis are presented only in the companion paper.

VEHICLES, FUELS AND CRANKCASE LUBRICANTS – Two 1998 model 1.8L GDI% Mitsubishi Carismas and two 1.6L PFI Carismas sourced from Germany were employed in this study. While the engines utilize the same basic block and displacement, the GDI power output is significantly higher than the PFI engine (92 versus 66 kW, respectively). Other pertinent differences are compression ratio (12.2:1 versus 10:1) and injection pressure (50 versus 3 bar). With the exception of the engines and mandatory equipment related to the engine option, all vehicles were identically equipped which included automatic transmissions and air conditioning.

A total of four fuels were tested. An unadditized base fuel meeting European Union year 2000 specifications is denoted F1. This fuel was chosen as being representative of base fuel properties in the European market where these vehicles are currently in use. Inspection data for the base fuel is given in Table 1. The same base fuel plus deposit control additives are denoted F2, F3 and F4. Fuel F2 was used in a half-fraction factorial design comparing

it to the base fuel (F1). The additive in F2 is a polyisobutylene amine dispersant/polyether fluidizer "synthetic" package. The additive in F3 is a polyetheramine and that in F4 is another synthetic package using a second type of polyisobutylene amine combined in a different ratio with a second polyether fluidizer. These latter two were tested in single demonstration runs to see if significant differences in performance between any of the chemistry types would be found. Between them they cover the majority of chemistry and package types in use in the North American and European marketplace. The doses chosen may be characterized as providing top tier intake valve and injector cleanliness in conventional PFI engines.

Table 1. Fuel Inspection Data

Density 15°	kg/m ³	0.7561
Reid Vapor Pressure	bar	0.57
Distillation ASTM D86		
IBP @	°C	33.8
10% vol @	°C	54.8
50% vol @	°C	102.6
90% vol @	°C	159.3
95% vol @	°C	175.9
FBP vol @	°C	195.8
Recovery	% vol	98.3
Composition ASTM D1319		
Saturates	% vol	57.8
Olefins	% vol	9.2
Aromatics	% vol	33.0
Sulfur ASTM D 2622	% mass	0.0119
Existent Gum	mg/100 ml	2.0
Washed Gum	mg/100 ml	0.6
Oxidation Stability	min	>980
Octane	Research	94.3
ASTM D 2699	Motor	83.8
F2 Additive	Polyisobutylene amine 1 + polyether fluidizer 1	
F3 Additive	Polyetheramine	
F4 Additive	Polyisobutylene amine 2 + polyether fluidizer 2	

A multipurpose 5W-30 API SJ/ILSAC GF-2 type crankcase oil, representing formulations predominant in the Japan market (where these vehicles have also been introduced) is denoted O1. A 10W-40 API SH/CF ACEA A3/B3-96 partial synthetic crankcase lubricant is denoted O2, representing the type of oil used in the European market. Both oils contain non-dispersant olefin copolymers as viscosity modifiers. The chemical profile of both fluids is listed in Table 2. These two oils are compared in the half-fraction matrix with F1 and F2, while F3 and F4 are tested exclusively with O2.

Table 2. Crankcase Oil Properties

	Oil O1	Oil O2
Treat Level (%wt)	10.1	14.2
TBN (mg KOH/gm)	5.5	9.5
Sulfated Ash (%wt)	0.67	1.2
Chemical Characteristics:		
(%wt) Calcium	0.152	0.31
Phosphorous	0.09	0.09
Sulfur	0.448	0.61
Zinc	0.105	0.10
Nitrogen	0.07	0.09
Magnesium	0	0

DRIVE CYCLES – A test is defined as accumulating 20,100 km by repetition of one of two specified drive cycles using one each of the defined fuels and lubricants from above. To ensure each drive cycle was reproduced consistently, the mileage was accumulated on a closed 12 km test track. The two multistage drive cycles, denoted "Rich" and "Lean" cycles, were developed to emphasize homogeneous and stratified charge operation, respectively, in the GDI vehicles while still representing a realistic mix of driving conditions (idle, urban, highway). Comparisons of the two cycles are presented in Table 3 and some representative operating data taken during mileage accumulation on each cycle is shown in Table 4. Some comparisons show similarities between the cycles, for instance the average speed and proportion of time spent in low speed (less than 45 kph, including idle), moderate (40-80 kph) and high (>80 kph) speeds. Other measures point out the differences in the cycles, such as the number and type of accelerations and load placed in the vehicles.

In addition to controls placed on the drive time of the vehicles, down time was also controlled. Vehicles were to be in operation for no more than 16 hours per day, and a 4 hour minimum continuous soak was included. Continuous unscheduled downtime (due to inclement weather, for instance) was limited to 24 hours if possible. Beyond that, a minimum "exercise" was to be instituted each day. Total elapsed time to accomplish the 20,100 km accumulation typically ranged from 22-28 days, though two runs took significantly longer.

Table 3. Rich and Lean Cycle Summary

Cycle		Rich	Lean
Speed	Idle	9%	27%
Distribution	<45 kph	34%	10%
	40-80 kph	25%	19%
	>80 kph	32%	44%
Average Cycle Speed		64 kph	61 kph
Acceleration	Type	Hard	Light
	accels/km	3.6	0.16
Ballast (kg)		230	0

Table 4. Typical Operating Data for GDI and PFI Vehicles on Rich and Lean Cycles

Engine		GDI		PFI	
Cycle		Rich	Lean	Rich	Lean
Time @ A/F	<14:1	21%	2%	30%	4%
	14<>20	47%	38%	65%	95%
	>20:1	32%	60%	5%	<1%
Avg. Temp (C)	Coolant	90	88	91	89
	Oil	98	89	99	89
	EGR	205	355	58	135
	Exhaust	533	390	525	415

EXPERIMENTAL DESIGN AND TEST MATRIX – The matrix of tests employed in this fleet trial is shown in Table 5. The goals of the program are to clearly distinguish the effects of factors:

- CYCLE – Rich versus Lean
- ENGINE – GDI versus PFI
- FUEL – F1 versus F2
- OIL – O1 versus O2

Because of the unknowns associated with the variability of the vehicles, particularly the new technology GDI vehicles, a fifth factor was taken into account:

- VEHICLE – car-to-car variation

Both GDI and PFI vehicles were run in a half-fraction factorial design on the variables CYCLE, VEHICLE and FLUID, where fluid is the combination of F1/O1 or F2/O1. Within GDI vehicles a full factorial minus one run (F1/O1;Rich) on CYCLE, FUEL and OIL was complete. The run using F2, O1 on the Rich Cycle was omitted. Duplicate runs in both vehicles allow us to estimate vehicle differences. (We chose to not confound vehicle with the interactions among the other factors by using it as blocking factor). The companion paper explains the design in more detail.

Fuels F3 and F4 were run in single demonstration tests to see if significant differences outside of those defined by fuels F1 and F2 would be observed.

Table 5. Mileage Accumulation Experimental Matrix

Vehicle	GDI #1	GDI #2	PFI #1	PFI #2
LEAN Cycle	F1/O1 F2/O1	F2/O2 F1/O2	F1/O1	F2/O2
RICH Cycle	F1/O1 F2/O2 F1/O2 F3/O2	F1/O1 F2/O2 F2/O2 F4/O2	F1/O1 F2/O2	F1/O1 F2/O2

VEHICLE PROCEDURE AND MEASUREMENTS
Prior to each test, the top end of the engine was rebuilt and the engine flushed clean. New inlet and exhaust valves were weighed and installed. Piston tops and cyl

der heads were scraped clean of deposit. The oil pan, valve cover coupons and intake manifold were cleaned and all deposits removed. PCV and EGR passages were checked for blockage. Cylinder heads were rebuilt using new valve stem seals and gaskets. New fuel injectors were flow checked using a 10 second continuous actuation on Stoddard solvent (PFI injectors at 3.1 bar, the same as vehicle operating pressure; GDI injectors at 5.2 bar, the maximum flow rig pressure) and installed. Paired camshafts were used on each vehicle so that precise wear measurements could be obtained after each run. Each GDI vehicle was assigned a pair of high pressure fuel pumps, one each for additized (F2, F3, F4) and base fuel (F1) runs to look for any long term wear patterns. A new air filter, oil filter (and triple oil flush), spark plugs and fuel filters were installed.

During mileage accumulation, 150 ml oil samples were taken at 4850, 9800 and 14,500 km intervals and retained for analysis. During the mileage accumulation data on engine rpm, vehicle speed and various engine temperatures (Coolant, oil sump, fuel tank, EGR and exhaust) are taken at one minute intervals. Representative A/F measurements were also taken of each cycle.

Performance Measurements – Prior to the start of mileage accumulation, each vehicle underwent performance tests on the fuel and lubricant to be tested to define the clean-engine (or "checkback," abbreviated C/B) baseline. At or near end of test the vehicles underwent the same tests (denoted EOT).

After engine rebuild and at the end of the 20,100 km mileage accumulation, a 21°C CRC Cold Start and Warmup (CS&W) driveability rating test (7) was performed. The rating was performed in an emissions test cell to control external variables. The CS&W also served as the preconditioning for the emissions tests to follow.

Emissions testing were performed in sequence with the CS&W driveability. European Union (EU) Urban and Extra-Urban (or High Speed) cycles (8) were run as first and second "bags," followed by a 10 minute soak and an "off cycle" test used in running-loss testing dubbed the "New York City Cab" (NYCC) cycle (9). The Urban cycle data presented here includes the 40 sec idle startup emissions, which are excluded in official procedure for certification tests. The NYCC cycle was chosen as it represented a cycle unlike either of the two reference cycles, with a high number of transitional maneuvers and more aggressive accelerations. A trace of the cycles is shown in Figure 1. Regulated emissions (hydrocarbon, carbon monoxide, nitrogen oxides) and fuel economy (via carbon balance) were obtained for each cycle (or "bag") as well as a weighted average. The three bag test above was performed in duplicate. Outlier criteria adapted from the Auto/Oil program (10) was used to determine whether a third run was needed for either all three tests or the more variable NYCC cycle alone.

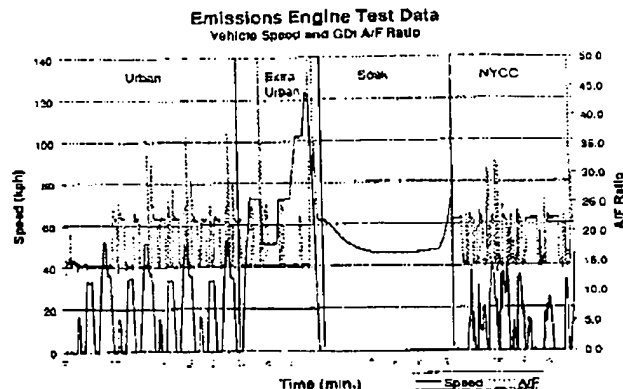


Figure 1. GDI Vehicle Emissions Cycle Trace

Particulate emissions measurements were also obtained. Two stage filter particulates were obtained for each bag. In addition, particulate size distribution was obtained on the total two day emissions using an eight plate MOUDI Impactor (11). Average plate mid-point collection size ranged from 10 micrometer to 20 nanometer.

At the beginning of test (following the C/B emissions) and after 18,500 km of mileage accumulation, 0-100 kph full throttle accelerations were performed. Ballasted and unballasted runs were completed (as in Table 3) on C/B, while only the condition being run for mileage accumulation was run at the 18.5K km mark. Six runs were averaged, three each in opposite directions on the test track. The runs were not performed at the end of mileage accumulation to avoid any influence on combustion chamber deposits that the full throttle accelerations might have (note this is only a concern from the standpoint of the Lean cycle; the Rich cycle used full throttle accelerations as part of the mileage accumulation).

Deposit Measurements – Upon completion of the 20,100 km accumulation and C/B performance tests, deposit measurements are performed. The crankcase lubricant is drained, weighed, and retained for analysis. The cylinder head is removed and disassembled and the inlet and exhaust valve deposits weighed, rated and photographed following the method used in the ASTM D 5500 procedure (12). Following photographs of each piston top and cylinder head, the thickness of the cylinder head and piston top deposits of each cylinder are determined using a commercial depth gauge. Five measurements are taken in each of eight mapped areas of the piston top and three of the cylinder head for GDI engines. Six mapped areas of the piston top and four of the cylinder head are used for PFI engines. The cylinder head and piston top deposits are then scraped and weighed.

The oil pan and valve cover coupons are rated for sludge and varnish. Cylinder wall acetate replicates are taken for analysis of cylinder wear. Fuel injectors are flowed to determine any change from C/B. Spark plugs are

removed and retained. The camshafts are removed and lobe roughness is measured.

DEPOSIT RESULTS

In the prior paper, it was noted that because of the run order chosen, it was possible that the preliminary deposit conclusions in GDI cars had a time factor bias, and that follow-up runs were planned to quantify or eliminate that possibility. Because of the nature of reusing the main engine parts, a time effect is always an unwelcome possibility in this sort of fleet work. The follow-up runs did in fact confirm a run order effect in the GDI cars for several of the deposit parameters. While this makes the analysis more complicated, due to the apparent linearity of the time trend it is possible to remove the bias from the data set.

In this paper, the run order effect observed with respect to deposits is accounted for by regressing the data on the independent variables (CYCLE, OIL, FUEL, ENGINE) along with run order as a covariate. Where run order is found to be statistically significant, the effect of run order can be estimated and removed, and the underlying true effect of the other parameters is more accurately gauged. The other advantage of modeling the results is that imbalances in the design (e.g. there are more Rich cycle runs than Lean cycle) are weighted appropriately. A summary of the model-predicted results for those parameters with a p-value of less than 0.1 (significant at a 90% confidence) are presented in Figures 2, 5 and 7 in the sections below and in Appendix A.

Note that PFI vehicle results are always analyzed in terms of FLUID (OIL plus FUEL) since they were deliberately confounded in the design. However, since PFI engine deposit mechanisms are fairly well understood, it is possible to ascribe most observed effects to either the OIL or FUEL.

INTAKE VALVE DEPOSITS—Of all the GDI deposit results affected, run order had the greatest influence on interpretation of intake valve deposit results in that a parameter which appeared to be significant in the prior work (Fuel) was now shown to not be a factor. Conversely, Oil, which was not identified as significant previously, is seen to be a significant factor in the amount of intake valve deposits formed in the GDI engine. These results are reflected in Figure 2, in which the European grade oil, O2, had a significant adverse impact on IVD relative to the Japanese market oil O1. Mechanistically, it makes sense that oil, and not fuel, should be the major factor. Oil has direct paths to the intake valves through the valve guides and PCV system, while fuel must be considered to interact with the intake valves in only a secondary fashion, such as through blowback upon intake valve opening. This result presents a challenge to the formulators of motor oil, as oil O2 is the superior performer in the areas of traditional crankcase performance (sludge, varnish, TBN retention, wear; see the companion paper for a full discussion).

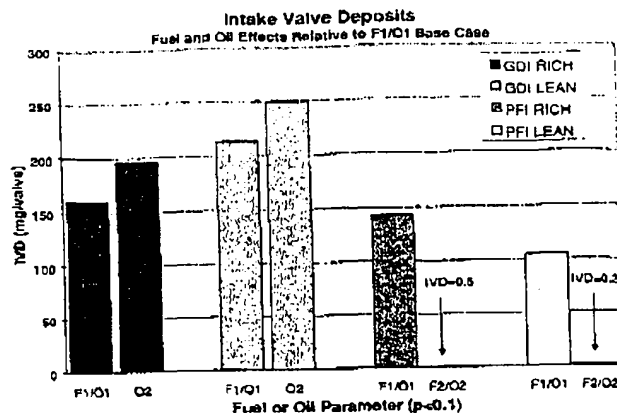


Figure 2. Statistically Significant Effects of Experimentally Varied Parameters on Intake Valve Deposits

Lean cycle operation generated significantly more deposits than Rich cycle in the GDI vehicles, and the majority of IVD (average of 75% and greater than 60% in every run) was accumulated on the even numbered (driver's side) intake valve of each cylinder. This was most pronounced in the Lean cycle operations, where even numbered valves accounted for more than 90% of deposits. Figure 3 presents a typical view of the heavily deposited valves. ICP (Inductively Coupled Plasma) analysis of the deposits show higher Ca, S and P on even numbered valves. This corroborates the theory that crankcase oil introduced via the PCV system, which is distributed only into the even numbered intake runners, is a major contributing mechanism to IVD in these engines. As seen in Figure 4, elements contained in the oil (Ca, S and P) exhibit a positive correlation with IVD, while wear metals (Fe (shown), Al and Cu) are negatively correlated with IVD which further supports the relation between IVD and oil.



Figure 3. 735 mg/valve GDI Intake Valve Deposit

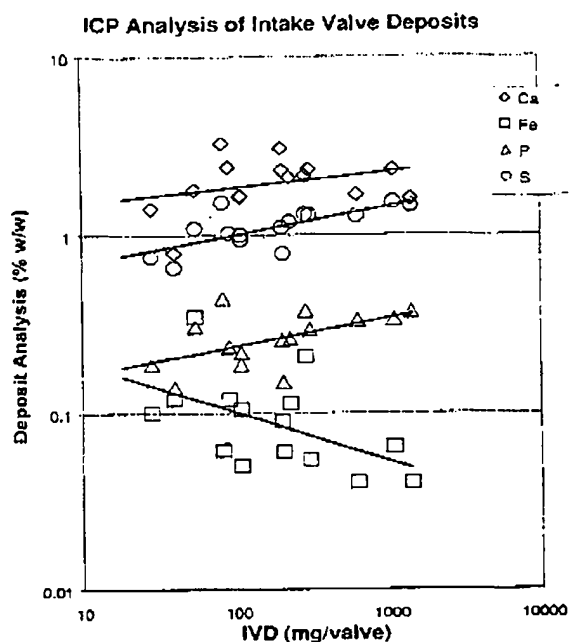


Figure 4. Elemental ICP Analysis of GDI Intake Valve Deposits

The IVD results are also instructive in showing the first contrasts between GDI and PFI technologies. IVD is unexpectedly higher in the GDI engines than the PFI, especially under Lean cycle conditions. This is unexpected in that IVD is primarily associated with the fuel in PFI engines, and with no (or very little) fuel expected to contact the valves in GDI engines, very little IVD would be predicted. However, as noted above, oil has direct paths to the intake valves but, without the washing of the fuel, limited means of removal.

Note the function of the deposit control additive in fuel F2 is clearly demonstrated in the PFI vehicle results, where IVD is reduced to essentially zero.

EXHAUST VALVE DEPOSITS – In both PFI and GDI engines exhaust valve deposits were an order of magnitude less than the intake valve deposits, averaging about 10 mg/valve. Run order was again significant in the GDI vehicles. All three additized fuels (F2, F3 and F4) produced higher EVD than F1, though the effect is only a change of about 5 mg/valve. CYCLE was the main significant effect found in the PFI vehicles; a significant fluid effect (favoring F1) could be seen during the rich cycle. One contrasting point between GDI and PFI exhaust valve deposits was in their appearance. PFI deposits were characteristically gray, while GDI deposits were sooty black.

INJECTOR DEPOSITS – Fuel injector flows and micrograph visualization were used to characterize injector

deposits. Figure 5 shows that fuel F2 produces significantly less flow loss in both GDI and PFI engines, though the only difference of any practical significance occurs in the GDI Lean case, where the difference in flow loss between additized and base fuel was about 6.5%. Visible proof of the difference between additized and unadditized fuel is seen in Figures 6a-d, showing typical examples of the injector barrel and plunger tip. It seems quite possible that, given a cycle tailored to injector deposits (for instance the ASTM D 5598 procedure (13)) and a more severe base fuel, injector deposits in the GDI could be much greater. Given the evidence to date, however, it appears the additive packages used in this study would be expected to successfully control injector fouling.

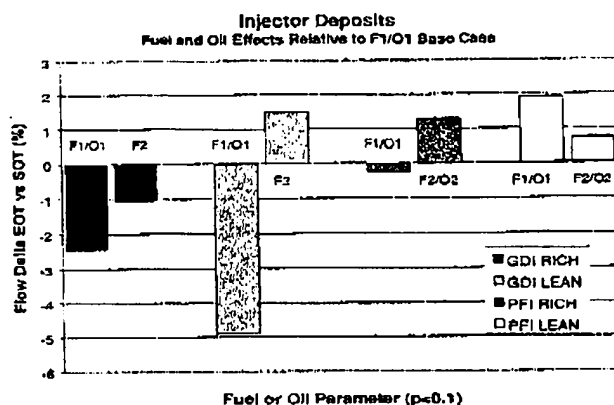
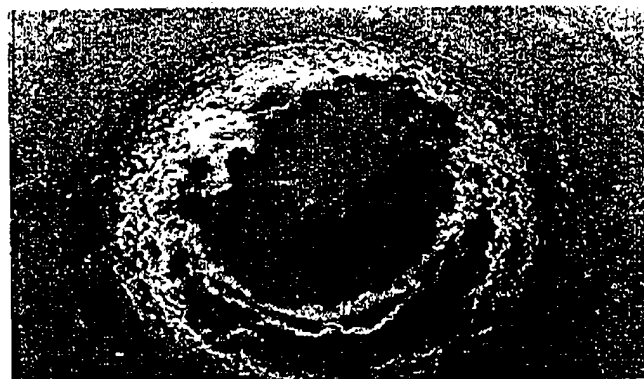


Figure 5. Statistically Significant Effects of Experimentally Varied Parameters on Injector Deposits (as Flow Loss at EOT)



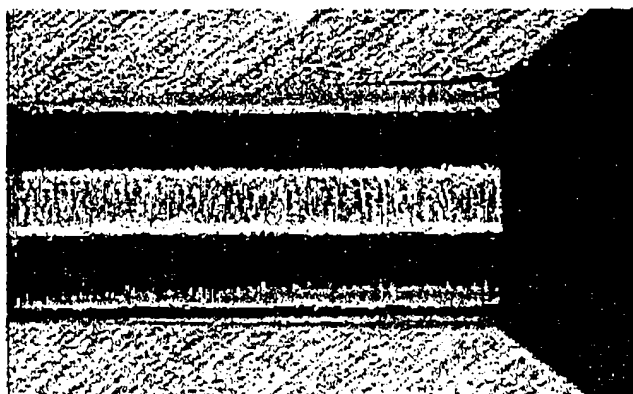
(a) Scanning Electron Microscopy of GDI Injector Plunger Tip, Head-On View, After 20,100 km on Lean Cycle Operation on F1 (Base Fuel)



(b) Injector Tip After 20,100 km on Lean Cycle Operation on F2 Additized Fuel



(c) Sectioned GDI Injector Body After 20,100 km on Lean Cycle on F1 Base Fuel

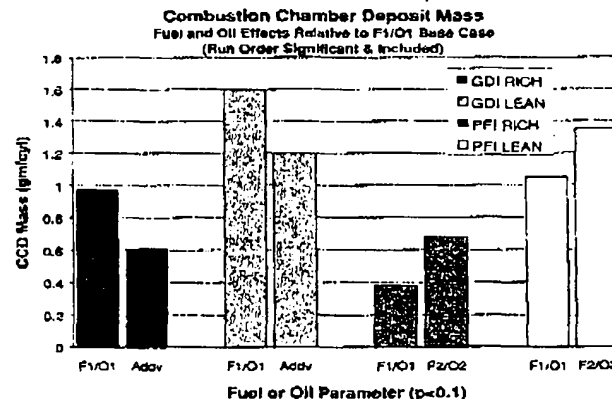


(d) Sectioned GDI Injector Body After 20,100 km on Lean Cycle on F2 Additized Fuel

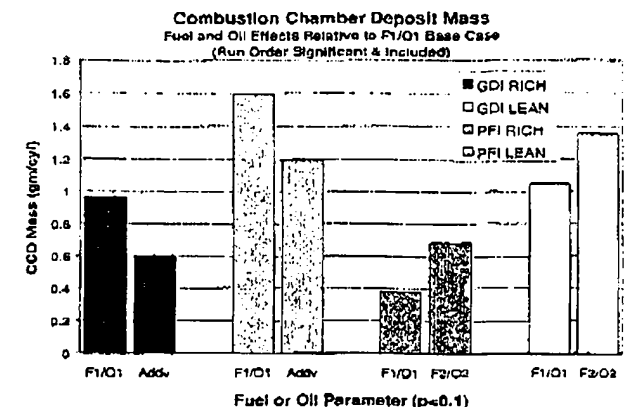
Figure 6. See Figures a,b,c and d above.

COMBUSTION CHAMBER DEPOSITS – Figures 7a-c present CCD mass, overall thickness and a more detailed breakdown of thickness, respectively. Note that while run order is significant in the GDI results, it does not alter the direction or prediction of the significant parameter effects. In both GDI and PFI engine types, cycle has a significant effect on the level of CCD produced, with the Lean cycle producing more deposits on the reference F1/O1 combination. Between engine types GDIs produce more CCD than PFIs under the same conditions.

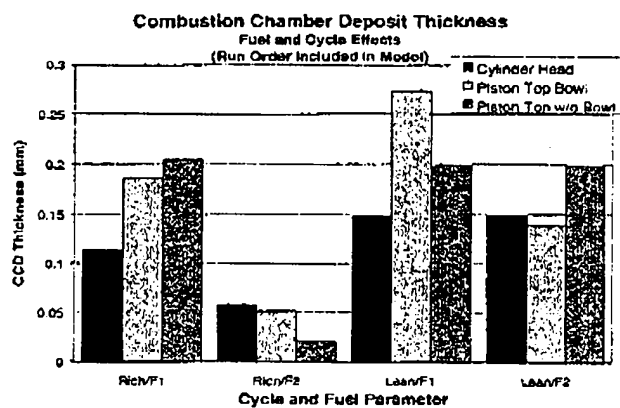
In the PFI engines, the Fuel F2/O2 can be seen to increase CCD relative to F1/O1, and this can likely be ascribed primarily to the fuel additive, though oil chemistry has also been shown to play a role in CCD. In the GDI engines, on the other hand, a larger effect in the opposite direction is seen which is significantly associated with Fuel. Across both deposit accumulation cycles, fuel F2 reduced CCD mass (Figure 7a). Overall (cylinder head plus piston top) CCD thickness differences (Figure 7b) however, are best described by Rich cycle operation alone. Though the trend is the same, no significant differences are calculated for the Lean cycle. To examine this further, we break down the components that make up the thickness measurement into piston top and cylinder head, and further divide piston top into bowl and piston top without bowl areas. The piston bowl is the area of the piston in which the fuel spray impacts during late injection timing.



(a) Statistically Significant Effects of Experimentally Varied Parameters on Combustion Chamber Deposit Mass



(b) Statistically Significant Effects of Experimentally Varied Parameters on Combustion Chamber Deposit Total Thickness



(c) The Effect of Fuel and Cycle on GDI Combustion Chamber Deposit Thickness

Figure 7. See Figures a, b and c above.

As seen in Figure 7c, F2 provides a significant decrease in CCD thickness in terms of all three measures in the Rich cycle and in the bowl thickness in the Lean cycle. Cylinder head and piston top without the bowl differences between F1 and F2 are not significant in the Lean cycle. Fuels F3 and F4 also significantly reduced piston top bowl thickness, but the other CCD data were inconclusive based on the single data comparison. ICP calcium in the deposits were mainly influenced by CYCLE, rather than OIL, confirming differences between O1 and O2 were not a significant factor.

EMISSIONS RESULTS

End of test (EOT; deposited engine) emissions are compared to checkback (C/B; clean engine) emissions in order to determine the effect of deposits overall. There

are many options possible even within that framework for making the comparison. In looking at the C/B data, it was observed that in most cases, there did not appear to be significant drift in the clean emissions of either vehicle type, but there was a significant amount of bounce in the GDI data. It was decided that since no significant run order effect was detected, average C/B results would be used for comparison with individual EOT results. It is believed that this yields a more precise estimate of clean engine emissions and a more accurate analysis. This also allowed us to overcome the operational problem of accounting for effects due to the differences in start-of-test fluids, such as the effect of crankcase oil O1 versus O2 on fuel economy.

There was, however, one case in which a step change in vehicle emissions behavior was observed. NYCC particulates jumped in both GDI vehicles after the fourth run (Figure 8 shows results in one vehicle). There are several interesting observations tied to this. First, the increase in NYCC particulates was accompanied by higher soot, pentane Insolubles and wear metals in the oil in the mileage accumulation, as is discussed in the companion paper. The NYCC cycle is very similar in character to the Rich Cycle for accumulation, which is the cycle the vehicles operated on for these runs. This may explain a tie between the particulate shift seen only in the NYCC emissions, but apparently carried over to the vehicle operation. Finally, note there was a scheduling stagger so that this effect did not take place at the same calendar time for each vehicle. At this point it is unknown what caused the shift.

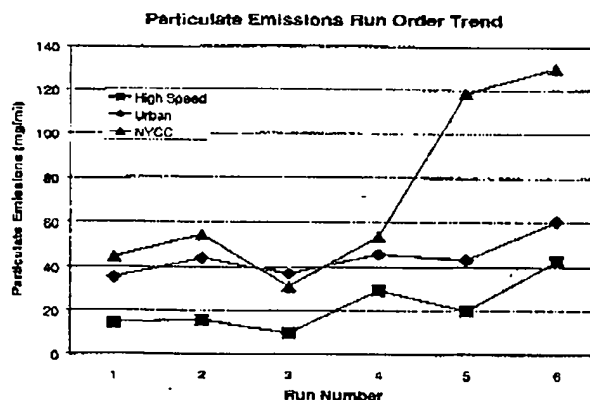
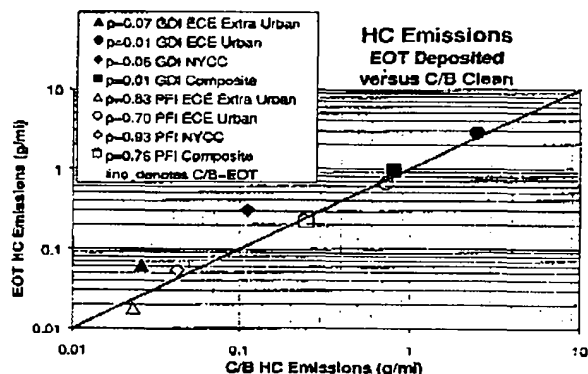


Figure 8. Particulate C/B Emissions Run Order Effect in a GDI Vehicle.

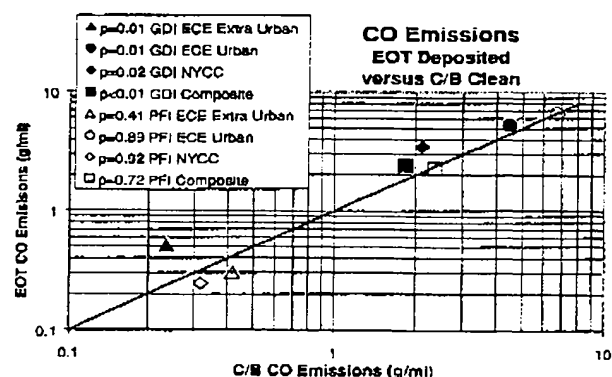
REGULATED EMISSIONS AND FUEL ECONOMY – Figure 9a-d present the results of the regulated emissions (hydrocarbon, carbon dioxide and nitrogen oxides) and fuel economy obtained from the emissions carbon balance. The format is chosen to provide a ready comparison of PFI and GDI, the different emissions cycles, and the effect of deposits between C/B and EOT. p-values of the significance of the delta between C/B and EOT

are provided in the legend. The p-value reported here is for the t-test used to assess whether the average EOT-C/B delta was significantly different from zero. Note that since PFI cars ran only a total of six tests compared to eleven for the GDI vehicles, the significance levels will be less for PFI given the same magnitude of effect. These results are also tabulated in Appendix B.

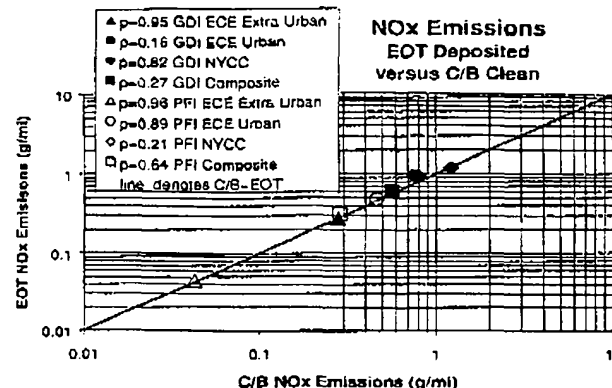
Hydrocarbon emissions (Fig. 9a) demonstrate a significant (at the $p < 0.1$ level) negative impact of deposits on the GDI vehicles for each cycle as well as the mileage-weighted composite. The NYCC cycle exhibits a particularly strong response with a three-fold increase between EOT and C/B (Note the percentage change for any of the emissions results are included in Appendix B). The GDI vehicles had higher HC emissions than the PFI vehicles, particularly the NYCC and Urban cycles (recall the Urban cycle here includes the 40 second start-of-test idle emissions). The PFI vehicles showed no statistically significant effect of deposits on HC emissions.



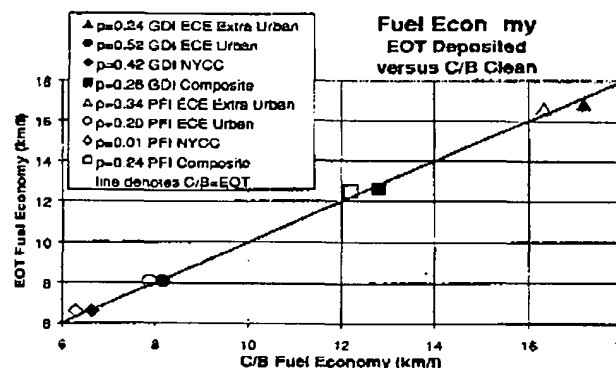
(a) Effect of Deposits on Hydrocarbon Emissions in GDI and PFI Vehicles



(b) Effect of Deposits on Carbon Monoxide Emissions in GDI and PFI Vehicles.



(c) Effect of Deposits on Nitrogen Oxides Emissions in GDI and PFI Vehicles.



(d) Effect of Deposits on Fuel Economy in GDI and PFI Vehicles.

Figure 9. See Figures a,b,c,d above.

The GDI vehicles also showed a strong response deposits with a 33% increase in composite CO and statistically significant differences between clean and deposited engines for each emissions cycle (Fig. 9b). The PFI cars again showed no response. In this case the two engine types had similar composite emissions levels though the individual cycle results, such as NYCC, did not always line up.

NOx emissions (Fig 9c) trended up by similar amount with deposits for both engine types (about 10% on the composite), but the differences were not statistically significant in either case. The PFI vehicles had lower NOx emissions than the GDI vehicles for each cycle.

While a summary of deposit versus fuel economy data yielded no statistically significant results (see Figure 9d legend), the trends observed are consistent across emission cycles and worth noting. Recall, first, that EOT fuel economy values are compared to the average C/B fuel economy on fresh oil of the same type (O1 or O2). A correction factor is applied to merge the data into the oil

point per emissions cycle shown. Also, while neither oil fell out of vis grade, there were some changes between beginning- and end-of-test oil properties that could affect fuel economy but are not accounted for here. However, analysis indicates oil vis effects were consistent across engine types so comparisons between GDI and PFI on a relative basis should be valid.

As can be seen in Figure 9d, PFI fuel economy trended up at EOT by about 2% on average. This value is consistent with previously reported increases associated with the buildup of CCD (e.g. 14), due primarily to increased thermal efficiency. The GDI vehicles, on the other hand, exhibited a trend of similar magnitude in the opposite direction; C/B fuel economy tended to be higher than EOT by about 2%. Interestingly, both PFI and GDI fuel economy did correlate with CCD mass at a 90% confidence level (with opposite-signed correlation coefficients). Clean vehicle fuel economy was somewhat greater for the GDI than PFI, but EOT fuel economy was essentially identical between the engine types. The difference in displacement and power output of the engines should be taken into account when making this comparison.

Individual Deposit Effects on Emissions – A summary of the statistically significant individual deposit type effects on GDI emissions is presented in Table 6. In the context of consistency, only the effect of injector fouling on NOx carries through to more than one emissions cycle. The Extra Urban cycle had the best repeatability of the emissions cycles used, which may account for the number of statistically significant results there. The PFI results, with fewer runs, show even fewer significant correlations. While it is somewhat disappointing that greater definition of the effects of the types of deposits could not be made, it is not unexpected for a scoping study such as this and will be the focus of future efforts.

Table 6. Summary of Individual Deposit Effects on GDI Emissions

Significance at p<0.10	Injector flow loss	IVD	CCD	
			Mass	Thick
Urban	-	-	-	-
Extra Urban	NOx	CO	HC, CO	HC, CO
NYCC	NOx	-	-	-
Composite	-	-	(FE)*	-

* Bracketed Values Indicate a Negative Correlation Coefficient

PARTICULATE EMISSIONS – Particulate emissions are currently the topic of intense study from a health effects

standpoint, particularly those of sub-micron size. Spark ignited gasoline engines have, for the most part, avoided this scrutiny as diesel engines tend to produce orders of magnitude more particulates. However, as can be seen in Figure 10, direct injection technology appears to produce substantially more particulate mass than conventional PFI, both in total mass and in the smallest size ranges. Both vehicles produced the bulk of their particulates in the smallest size range, with more than a third of PFI and nearly half of GDI particulate mass collected in the 20 nm range on average. The data in the figure represents an average over the first six runs on each engine technology for each of the plates in the MOUDI impactor.

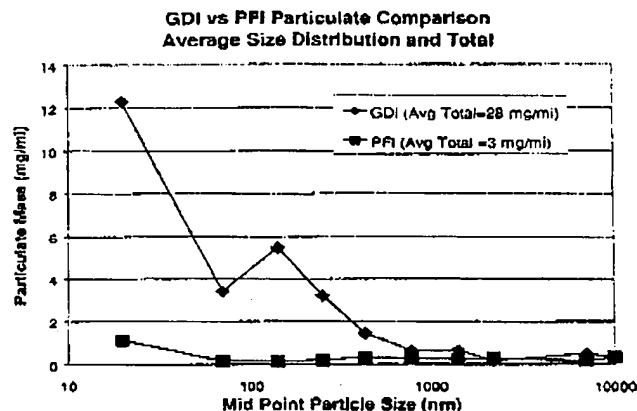
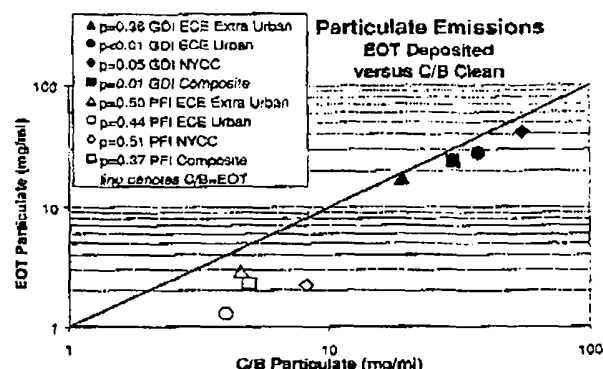
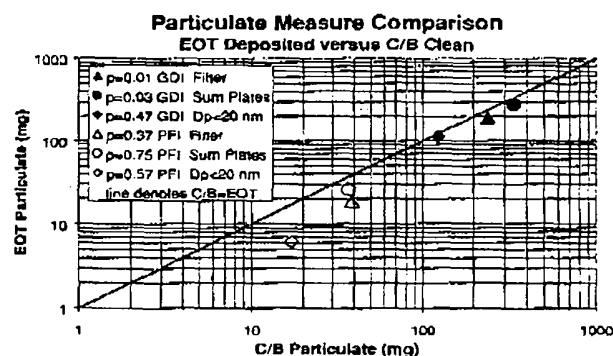


Figure 10. Characterization of Particulate Emissions in GDI and PFI Vehicles.

Figure 11a presents the EOT and C/B particulate results from the two-stage filter for the different emissions cycles. Figure 11b presents composite particulate data from the two-stage filter, the sum of the MOUDI plates, and the results of the final (20 nm) collection plate. The data is compelling in that the deposited, EOT engines produced significantly less particulates than the clean, C/B engines, both overall and in the 20 nm range. The trend is the same for both engine types, though only the GDI data with more runs is statistically significant. Note the three particulate measures gave consistent results in terms of the trends. In diesel studies, a NOx/particulate tradeoff is commonly attributed to thermal efficiency; in the GDI a similar tradeoff appears to be occurring. The trend downward in fuel economy is counter to this theory, but could be the result of conflicting effects such as fuel absorption in the piston bowl deposits, IVD restriction of intake air flow, etc.



(a) Effect of Deposits on Particulate Emissions in GDI and PFI Vehicles.



(b) Effect of Deposits on Particulate Emissions; by Collection Method and Size.

Figure 11. See Figures a and b above.

ACCELERATION – The performance advantage of the GDI engine is clearly shown in Figure 12, in which GDI-equipped cars are 1-2.5 seconds faster in 0-100 kph full throttle acceleration than the PFI-equipped cars. Ballasted data refers to that collected with the 230 kg placed in the vehicles for Rich cycle runs. Unballasted accelerations had no extra weight, as in Lean cycle runs. This figure also shows the significant negative effect deposits have on the GDI performance.

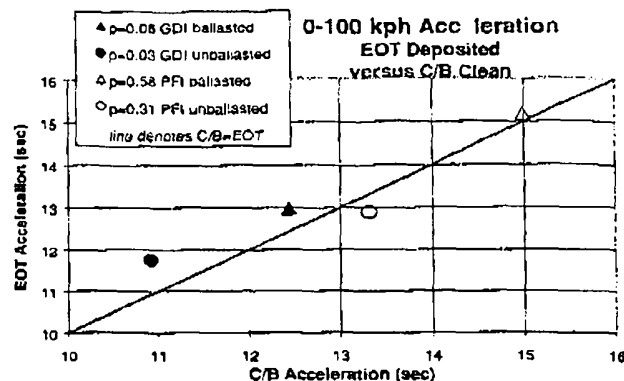
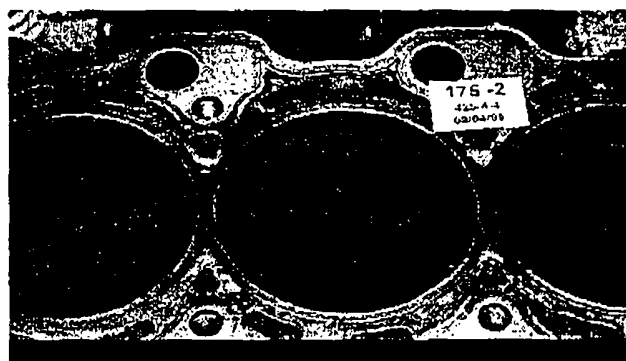
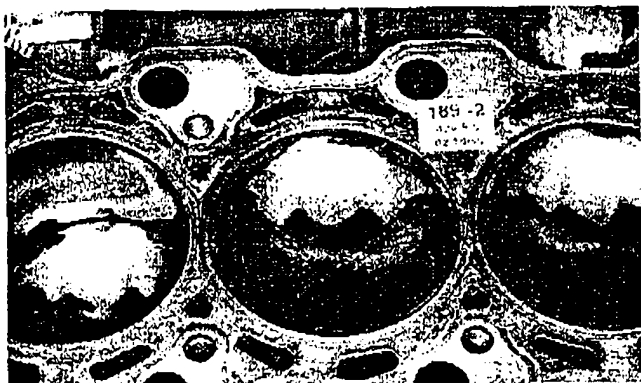


Figure 12. Effect of Deposits on Acceleration Time in GDI and PFI Vehicles.

An Experiment into the Relation between CCD and Acceleration – As in most of the emissions results above, acceleration performance did not significantly correlate with any of the individual deposit types. In order to investigate the mechanism of CCD formation and removal and to see if data directly connecting CCD and acceleration in the GDI vehicle could be obtained, a follow-on experiment was performed at the end of one of the 20,100 km test runs.



(a) GDI Cylinder Head CCD Following 20,100 km Rich Cycle Mileage Accumulation on Fuel F4



(b) GDI Cylinder Head CCD Following 1600 km Additional Mileage Conditioning on Fuel F4 and 1100 km on a High Dose of the F3 Fuel Additive.

Figure 13. See Figures a and b above.

Figure 13a is a photo taken at the end of 20,100 km test, which used F4/O2 on the Rich cycle. Following measurement, the engine was reassembled with all deposits intact and sent back out for 1600 km accumulation on the Rich cycle and same fuel to recondition deposit stability. The vehicle then ran an additional 1100 km (about two tanks of fuel) on an "aftermarket" dose of the polyether amine additive used in Fuel F3 (an order of magnitude up-treat). This type of additive is known to reduce combustion chamber deposits in PFI engines at such doses. The engine was disassembled, the deposits remeasured and the photo in Figure 13b taken. The piston bowl (the area directly in line with the injector fuel spray) experienced a 100% deposit removal. Overall the deposit thickness decreased about 30%. In order to assure this result was not simply due to the procedure, the process was repeated, but without adding the polyether amine. At the end of that 2700 km mileage accumulation, it could be seen that the CCDs were reestablishing at near the original levels. The lower portion of Figure 14 presents this data.

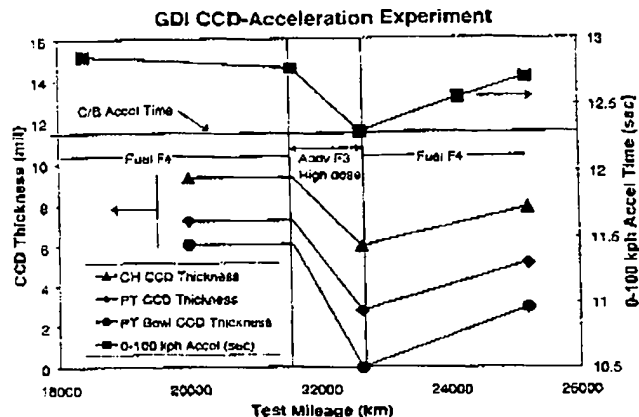


Figure 14. Comparison of the Change Observed in CCD Thickness and GDI Vehicle Acceleration Performance.

Also shown in Figure 14 are 0-100 kph accelerations performed during this experiment. The usual 18,500 km acceleration before EOT teardown was followed by one at the end of the 1600 km reconditioning run, with virtually the same result. At the end of the 1100 km "two tank" accumulation, before teardown, another acceleration was run with statistically lower times. During the final 2700 km phase of mileage accumulation and at the same mileage points (1600 and 2700 km) as the previous sequence, accelerations were again performed. As seen in the figure, the acceleration times directly track with the change in measured CCD thickness. This would appear to be a confirmation that CCD plays a direct role in the deposit/acceleration relationship.

DRIVEABILITY – Both GDI and PFI technology vehicles performed well in CRC Cold Start & Warmup tests throughout the program. There was no statistically significant change in driveability demerits with either engine type, and the level of demerits recorded was below what is considered objectionable to consumers. Several factors may be considered in future work to test the appetite and requirements of the vehicle. One parameter to consider is the fuel, which in this study had relatively low (good) driveability index. Use of a more severe, less easily volatilized fuel may show more sensitivity.

FUTURE WORK

1. Further refine mileage accumulation cycles to best discriminate the effects of fuel additive and crankcase oil on the various GDI deposits; continue to look for fuel additive and crankcase oil solutions to deposit buildup.
2. Run further experiments to separate the effects of individual deposit types (injector, IVD, CCD) on vehicle performance (emissions, driveability, acceleration).

3. Determine root causes of the effect of run order on deposits and oil performance.
4. Expand the investigation into other direct injection gasoline engine designs.

SUMMARY

An ambitious scoping study was undertaken to gain insight into the fuel and oil appetites, deposit formation characteristics and effects on vehicle performance of direct injection gasoline engine technology. Though run order effects had to be taken into consideration, through statistical modeling the study has yielded a number of significant insights.

With respect to engine deposits:

1. Intake valve, combustion chamber and injector deposit formation in GDI engines is greater than those in the comparable PFI technology engine.
2. CCD and injector deposits in DGI engines are found to be a function of mileage accumulation cycle and fuel, but not crankcase oil. The additives used in this study proved to be effective in controlling deposits, as injector deposits did not form and CCD was lowered compared to base fuel.
3. Using the complete data set and deposit analysis, IVD in GDI engines is found to be dependent on crankcase oil and cycle, but not fuel. This clarifies the preliminary results presented by the authors in a previous paper. The 5W30 GF-2 oil produced higher levels of IVD in the GDI engine than the 10W-40 ACEA oil. IVD in PFI engines were completely eliminated using the synthetic fuel additive, regardless of cycle.
4. The best discrimination between oil and fuel parameter effects was cycle specific for injector deposits (Lean) and combustion chamber deposits (Rich).
In terms of performance effects:
5. In GDI vehicles, deposited engines were found to have increased hydrocarbon and carbon monoxide emissions and poorer fuel economy and acceleration, but lower particulate emissions at a statistically significant level. Effects in PFI engines, though in general not statistically significant, were directionally the same for NOx and particulates but the opposite for HC and CO emissions and fuel economy
6. In terms of specific deposit effects, evidence is presented that CCD is correlated with acceleration, HC and CO emissions and fuel economy, while injector deposits correlate with NOx formation in the GDI engine.

ACKNOWLEDGMENTS

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APPENDIX

Appendix A. Summary of Engine Deposit Analysis						
Deposit Measure	Value	Engine Type	Parameter Effect	p-value for significance of effect	Parameter Combination	Model Value (at 1st run if necessary)
Injector Deposit	% flow restriction	GDI	Additized Fuel	0.001	Rich/Unadd	2.42
			Cycle	0.87	Rich/Add	1.03
			Cycle x Fuel	0.01	Lean/Unadd	4.8
					Lean/Add	-1.6
		PFI	Cycle	0.2	Rich/O1=F1	0.24
			Oil&Fuel	0.72	Rich/O2=F2	-1.3
Intake Valve Deposit	mg/valve	GDI	Cycle x Oil&Fuel	0.08	Lean/O1=F1	-1.92
			Run order	0.0001	Rich/O1	160.2
			Cycle	0.03	Rich/O2	196.6
			Oil	0.0001	Lean/O1	213.5
			Vehicle	0.025	Lean/O2	249.9
		PFI	Cycle	0.07	Rich/O1=F1	143.1
			Oil&Fuel	0.0001	Rich/O2=F2	0.45
					Lean/O1=F1	105.4
					Lean/O2=F2	0.2
Exhaust Valve Deposit	mg/valve	GDI	Run order	0.01	F1	5.1
			F2	0.01	F2	8.4
			F3	0.01	F3	10.9
			F4	0.003	F4	12.9
		PFI	Oil&Fuel	0.13	O1=F1	12.89
					O2=F2	18.16
Combustion Chamber Deposit Mass (Piston Top + Cylinder Head)	mg/cylinder	GDI	Run order	0.04	Rich/Unadd	0.97
			Cycle	0.001	Rich/Add (F2 or F3)	0.61
			Additized Fuel	0.01	Lean/Unadd	1.8
					Lean/Add (F2 or F3)	1.2
		PFI	Cycle	0.02	Rich/O1=F1	0.381
			Oil&Fuel	0.11	Rich/O2=F2	0.684
					Lean/O1=F1	1.0504
					Lean/O2=F2	1.3539
Combustion Chamber Deposit Thickness (Piston Top + Cylinder Head) excluding F3 and F4	mm	GDI	Run order	0.001	Rich/F1	0.236
			Cycle	0.001	Rich/F2	0.13
			F2 on Rich	0.004	Lean/F1	0.305
					Lean/F2	0.305
		PFI	Cycle	0.01	Rich/O1=F1	0.074295
			Oil&Fuel	0.07	Rich/O2=F2	0.13335
					Lean/O1=F1	0.1908175
					Lean/O2=F2	0.249936
Combustion Chamber Deposit Thickness Cylinder Head excluding F3 and F4	mm	GDI			Lean/F2	0.1602
			Run order	0.08	Rich/F1	0.1141
			Cycle	0.025	Rich/F2	0.059
			F2 on Rich	0.086	Lean/F1	0.1492
		PFI				
			Run order	0.05	Rich/F1	0.1495
			Cycle	0.035	Rich/F2	0.1035
			F2 on Rich	0.03	Lean/F1	0.1602
Combustion Chamber Deposit Thickness Piston Top without Bowl excluding F3 and F4	mm	GDI			Lean/F2	0.1492
			Run order	0.37	Rich/Unadd	0.186436
			Cycle	0.02	Rich/Add	0.051816
			Additized Fuel	0.003	Lean/Unadd	0.273912
		PFI			Lean/Add	0.139446
					Rich/F3 measured	0.091
					Rich/F4 measured	0.16

APPENDIX

Variable	Subset	Engine Type	Measured Value		EOT vs C/B		p-values for difference between engine type	
			C/B (Clean)	EOT (Deposited)	Delta	%	@C/B	EOT and C/B
0-100 kph Acceleration (sec)	Ballasted	GDI	12.43	12.98	0.55	4.4%	<.001	0.056
	Unballasted		10.91	11.75	0.84	7.7%	<.001	0.030
	Ballasted	PFI	14.99	15.18	0.19	1.3%		0.580
	Unballasted		13.31	12.89	-0.42	-3.2%		0.309
Fuel Economy (km/l)	ECE High Speed	GDI	17.19	16.90	-0.69	-4.0%	0.01	0.24
	ECE Urban		8.18	8.10	-0.18	-2.2%	0.16	0.520
	NYCC		6.65	6.58	-0.15	-2.2%	0.29	0.420
	Wtd		12.83	12.83	-0.45	-3.5%	0.002	0.280
	ECE High Speed	PFI	16.33	16.66	0.76	4.7%		0.340
	ECE Urban		7.89	8.10	0.51	6.5%		0.200
	NYCC		6.30	6.59	0.68	10.7%		0.014
	Wtd		12.22	12.51	0.67	5.5%		0.240
CO Emissions (gm/km)x1.6	ECE High Speed	GDI	0.24	0.51	0.28	118.0%	0.2	0.011
	ECE Urban		4.49	5.30	0.82	18.2%	0.05	0.014
	NYCC		2.12	3.49	1.37	64.8%	0.13	0.018
	Wtd		1.84	2.44	0.61	33.1%	0.11	0.004
	ECE High Speed	PFI	0.42	0.31	-0.11	-26.9%		0.410
	ECE Urban		6.73	6.68	-0.05	-0.8%		0.890
	NYCC		0.32	0.25	-0.07	-23.0%		0.920
	Wtd		2.37	2.28	-0.09	-3.7%		0.720
THC Emissions (gm/km)x1.6	ECE High Speed	GDI	0.03	0.08	0.04	138.2%	0.7	0.070
	ECE Urban		2.50	2.88	0.38	15.4%	0.03	0.015
	NYCC		0.11	0.30	0.19	176.8%	0.09	0.060
	Wtd		0.81	0.97	0.17	20.8%	0.03	0.010
	ECE High Speed	PFI	0.02	0.02	-0.01	-23.4%		0.830
	ECE Urban		0.73	0.68	-0.07	-10.1%		0.700
	NYCC		0.04	0.05	0.01	26.1%		0.930
	Wtd		0.25	0.22	-0.02	-9.7%		0.760
NOx Emissions (gm/km)x1.6	ECE High Speed	GDI	0.28	0.28	0.00	0.6%	<.001	0.950
	ECE Urban		0.77	0.95	0.18	23.8%	0.23	0.16
	NYCC		1.22	1.20	-0.02	-1.6%	0.09	0.820
	Wtd		0.57	0.62	0.06	9.7%	0.04	0.270
	ECE High Speed	PFI	0.04	0.04	0.00	4.4%		0.960
	ECE Urban		0.46	0.49	0.02	4.8%		0.89
	NYCC		0.80	0.95	0.15	19.5%		0.210
	Wtd		0.29	0.32	0.03	10.9%		0.640
PARTICULATES Filter Plate Measure (mg/km)x1.6	ECE High Speed	GDI	19.13	17.50	-1.62	-8.5%	0.008	0.380
	ECE Urban		38.07	28.17	-9.90	-26.0%	0.009	0.001
	NYCC		55.48	42.16	-13.31	-24.0%	0.01	0.05
	Wtd		30.40	24.47	-5.93	-19.5%	0.002	0.010
	ECE High Speed	PFI	4.53	2.94	-1.59	-35.1%		0.500
	ECE Urban		3.88	1.28	-2.71	-68.0%		0.44
	NYCC		8.13	2.23	-5.90	-72.6%		0.510
	Wtd		4.89	2.31	-2.58	-52.7%		0.370
PARTICULATES MOUDI Impactor (mg/km)x1.6	Sum of Plates	GDI	337.63	281.31	-56.32	-16.7%	0.004	0.030
	Sum of Plates	PFI	37.33	25.73	-11.60	-31.1%		0.750
	Dp<20 nm	GDI	123.25	113.75	-9.50	-7.7%	0.007	0.470
	Dp<20 nm	PFI	17.17	6.17	-11.00	-64.1%		0.570

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A Method for Suppressing Formation of Deposits on Fuel Injector for Direct Injection Gasoline Engine

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ABSTRACT

Our concern was with the phenomenon of the fuel flow rate change in the injector due to deposit formation in the direct injection gasoline engine. The fundamental factors in the deposit formation on the nozzle were investigated, and engine dynamometer tests were performed. It was clarified that the residual fuel in the nozzle hole should be kept in a liquid state so that deposit precursors could be washed away by fuel injections. As a consequence, the nozzle temperature had to be below the 90 vol. % distillation temperature of the fuel, which was the most important index to suppress the deposit formation.

INTRODUCTION

It is well known that the accumulation of deposits on the nozzle in a fuel injector changes the flow rate and the spray characteristics, so that the engine performance becomes deteriorated. The suppression of the deposit formation on the nozzle has been examined previously for multiport fuel S.I. engines and diesel engines before (1)(2)(3)(4). Recently, direct injection gasoline engines have been developed which have successfully improved fuel economy under ultra lean stratified combustion (5)(6)(7). The nozzle in the fuel injector for the direct injection gasoline engine is exposed to high temperature combustion gas and soot. In such a rigorous environment, it is predicted that deposits easily accumulate on the nozzle. The fuel injection pressure, the fuel properties and the combustion processes of the direct injection gasoline engines are also greatly different from those of the diesel engines. It is thought that the factors in the

deposit formation on the nozzle can be classed into such as two groups. One factor is the combustion products, such as soot, which are generated in the combustion chamber. The combustion products may accumulate on the nozzle surface and invade the nozzle hole. The other factor is the residual fuel on the nozzle. The residual fuel may change in quality due to thermal factors. These factors will be influenced by the compositions and the temperatures of the combustion gas and the fuel. Therefore, the formation processes of the deposits on the nozzle are very complicated, and they have not yet been clarified in detail.

EXPERIMENTAL APPARATUS AND PROCEDURES

The constitution of the injector used in this study is described (8). The nozzle in the fuel injector had an injection hole with a diameter of 0.2 mm and a port type swirl. This fuel injector could operate at a maximum fuel pressure of 12 MPa and had a fuel flow rate of 8 mm³/ms. The Sauter Mean Diameter (SMD) of the fuel spray droplets was 15-20 μm, and the angle of the spray shape was 60 degrees at atmospheric pressure. This nozzle was made of stainless steel (AISI 440C) with a surface hardness of HRC60 and a surface roughness of 0.04 μm Ra.

Engine dynamometer tests were performed to examine the deposit formation using two kinds of engines with the above-mentioned injectors. One was an in-line 4-cylinder engine, and the other was a single-cylinder engine, which was improved for these experiments.

The in-line 4-cylinder engine was used to examine under which conditions the fuel flow rate in the injector decreased due to the deposit accumulation. The specifications of the in-line 4-cylinder engine are shown in Table 1. The engine speed was set at 1000-4000 rpm, and the fuel flow rate was set at 15-50 mm³/st (mm³ per stroke of the needle valve in an injector) in these tests. The gasoline used was unleaded regular with a Research Octane Number (RON) of 91. Each test with the in-line 4-cylinder engine was performed for 6.5 hours.

Table 1. In-line 4-cylinder engine specifications

Displacement	1998 cc
Bore x Stroke	86 x 86 mm
Valves per Cylinder	4
Compression ratio	10
Intake port	Helical and Straight
Fuel pressure	12MPa
Fuel supply	Swirl injector
Fuel	Unleaded regular (91RON)

Table 2. Single-cylinder engine specifications

Displacement	433cc
Bore x Stroke	82 x 82 mm
Compression ratio	8
Engine speed	1000rpm
Fuel pressure	6MPa
Fuel pressure	Swirl injector
Fuel supply	Unleaded regular (91RON)

The single-cylinder engine was used to investigate the processes of accumulation of the deposits on the nozzle; the specifications are shown in Table 2. Although the same type injectors were used in the single-cylinder engine, the displacement, bore, stroke and compression ratio in this engine were slightly different from those of the in-line 4-cylinder engine. The single-cylinder engine speed was fixed at 1000 rpm. The fuel pressure was regulated at 6 MPa because the deposit accumulation process was hastened. In this engine head, the coolant water passages were independently arranged around the nozzle circumference to control the temperature of the nozzle. The nozzle temperature was measured by a thermocouple whose diameter was 0.25 mm and whose position was 1 mm away from the injection hole. Each test with this single-cylinder engine was performed for 30 hours.

The flow rate change in the injector was evaluated by measuring the static flow rate in the injector before and after the engine dynamometer test. The air/fuel ratio in the exhaust gas was also measured in these engine tests, and we confirmed the correlation between the changes in the fuel flow rate and the air/fuel ratio.

EXPERIMENTAL RESULTS AND DISCUSSIONS

FACTORS IN DEPOSIT FORMATION – To examine the factors in deposit formation, engine dynamometer tests were performed on the in-line 4-cylinder engine. The engine was run for 6.5 hours under each condition. As shown in Fig. 1, the fuel flow rate in the injector noticeably decreased under the conditions of 3000 rpm to 4000 rpm and the 30 mm³/st neighborhood. The relation between the engine driving conditions and the nozzle temperature is also shown in Fig. 2. The conditions under which the nozzle temperature exceeded 150°C coincided with the conditions under which the fuel flow rate was noticeably decreased. The deposit accumulated in the nozzle hole was strongly adhered on the surface. It had to be rubbed with a metal piece to remove the deposits from the nozzle hole.

We observed the outside surfaces and the injection holes of the nozzles by an optical microscope after the in-line 4-cylinder engine tests. The nozzle surface with the much changed flow rate was found to be covered by a deposit layer and the layer extended into the injection hole.

The layer accumulated on the nozzle surface was very fragile and fell off the nozzle surface easily when it was touched with a finger. The compositions of the deposits on the nozzle surfaces were analyzed by Electron Probe Micro Analysis (EPMA) and infrared spectra analysis and the following results were found. The major constituents of the deposits were 15-30 % carbon and 1-5 % oxygen, and the phosphorous and calcium contained in the engine oil which only existed at less than 0.5 %. Aromatic groups (C=C ring), carbonyl groups (C=O), hydroxyl groups (O-H) and alkyl groups (C-H) were confirmed as major functional groups. Based on these analyses, it was recognized that the deposits were mainly constituted of functional groups with abundant oxygen which composition was similar to that of the deposits in combustion chambers of gasoline engines. In addition the carbonization degree of the deposits on the nozzle surface was lower than the carbonization degree of soot in diesel engines.

The deposit layer was the thickest at the exit of the nozzle hole, and the layer became progressively thinner toward the upper part of the nozzle hole. Because the amount of the deposits in the nozzle hole was very slight, we could not plainly specify the chemical structure.

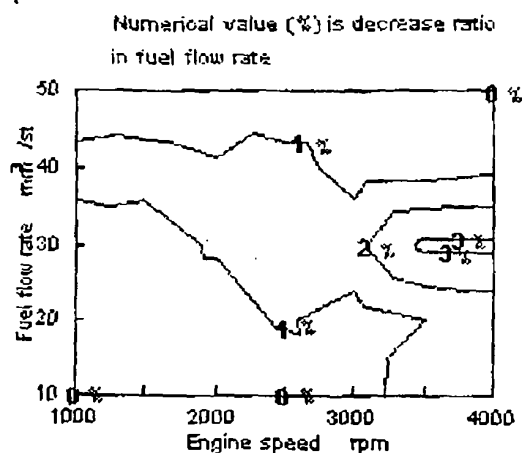


Fig.1 Relation between decrease ratio in fuel flow rate and engine test conditions

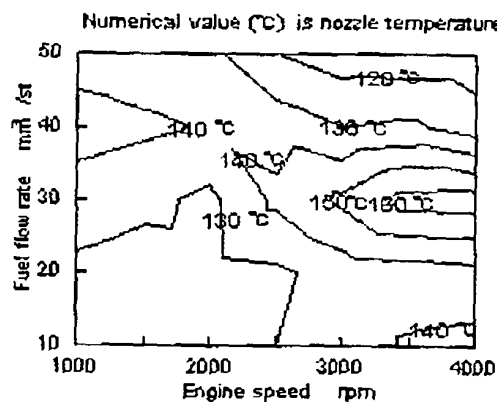


Fig.2 Relation between nozzle temperature and engine test conditions

Moreover, to examine the effects of the fuel properties, the 4-cylinder engine tests were performed with 7 kinds of fuels. Under each condition, the engine was run for 6.5 hours at 3500 rpm and 30 mm³/st, and the nozzle temperature was 160°C. We measured the properties of the fuels, which are the vapor pressure, 50 vol. % distillation temperature, 90 vol. % distillation temperature, endpoint, aromatic component ratio, moisture ratio and gum amounts. Table 3 shows these characteristic values of the properties with F1-F7 fuels. The correlation coefficients between these fuel characteristic values and the ratio of decrease in the fuel flow rate are shown in Fig. 3. It was found that the correlation coefficient between

the 90 vol. % distillation temperature and the decrease ratio in the fuel flow rate was the highest at 0.93. The correlation coefficients of the 50 vol. % distillation temperature and the endpoint were higher, too. Taken in the light of these correlation coefficients, the fuel flow rate change due to the deposit accumulation was related to the distillation characteristics of the fuel. However, the correlation coefficient for the aromatic content was very low.

Table 3. Fuel specifications

	F1	F2	F3	F4	F5	F6	F7
Vapor pres. (kPa)	78.1	73.3	57.6	82.9	82.8	58.3	77.3
T50% point (°C)	95.0	98.5	107	85.5	85.5	122	91.0
T90% point (°C)	165	163	144	147	148	168	143
Endpoint (°C)	184	185	187	190	194	204	180
Aromatic cont. (%)	29.6	33.1	50.3	25.3	23.2	37.3	39.4
Gum cont. (mg/100ml)	0.64	0.96	1.19	0.20	18.3	0.41	16.5
Water cont. (ppm)	63.6	74.2	144	63.9	49.2	73.0	182

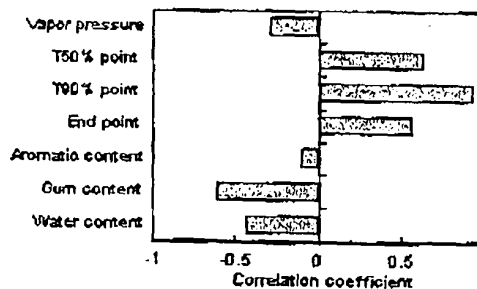


Fig. 3 Correlation coefficient between fuel specification and decrease ratio in fuel flow rate

ACCUMULATION PROCESS OF DEPOSITS – The single-cylinder engine tests were performed to investigate the accumulation process of the deposits on the nozzle in detail. Driving conditions A-E of these engine tests are shown in Table 4. The nozzle temperature shown in this table was the value at 30 minutes after the start of the engine test. Two kinds of unleaded regular gasoline were used in these tests; the 90 vol. % distillation temperatures of these fuels were 150°C and 168°C.

Condition A had the highest temperature of the nozzle and air/fuel ratio 12. B is the same engine driving condition as A, but the nozzle of B is cooled by water, whose temperature is 100°C. In the case of D, the nozzle temperature is almost the same as that of C, but soot is generated in C. Under condition E, using another fuel which contains higher boiling point ingredients than the fuel used in A-D, E was examined under the same engine driving condition as A.

Figure 4 shows the fuel flow rate changes with time under the condition A-D. In condition A, whose temperature was the highest, at least, the flow rate change became the largest under all conditions at 30 hours. However, the flow rate change did not occur from the start to several hours, and it began to decrease at around 2 hours from the start. Although the decrease in the flow rate continued up to around 8 hours, it did not change much after 10 hours. In condition B, whose temperature was the lowest, the flow rate change was the lowest, too. There is not much difference between the flow rate changes in C and D. The results show that soot occurring in the combustion chamber does not always lead to changes in the fuel flow rate. Under all conditions, the flow rate changes did not occur from the start to several hours; moreover, they did not change much after 10 hours.

The relation between the nozzle temperatures and the fuel flow rate changes in the injectors for the single-cylinder engine is shown in Fig. 5. From the results of A-D, it was found that the flow rate change increased as the nozzle temperature became higher. When the nozzle temperature exceeded 160 °C, the flow rate change became significantly greater. It is thought that this phenomenon is connected to the distillation characteristics of the fuel. Using another fuel, containing higher boiling point ingredients than the fuel used in the tests of A-D, tests conducted under the same engine driving condition as A gave the result shown as E. When the fuel with a higher boiling point ingredient was used, the flow rate change became smaller than that in A. The results show that the flow rate change due to the deposit accumulation is related to the nozzle temperature and the evaporation characteristics of the fuel. The 90 vol. % distillation temperatures of 2 types of fuels used for these engine tests are shown by the broken line and the dotted line in this figure. It was observed that the flow rate change was restrained when the nozzle temperature was lower than the 90 vol. % distillation temperature of the fuel.

The accumulation processes of the deposits were observed using a SEM. Figure 6 is a photograph of the nozzle, for which the fuel flow rate decreased 10 % after 30 hours under condition A. A smooth and uniform deposit layer covered the nozzle surface. A hollow existed around the nozzle hole, which contained some lumps of deposits like coral on the circumference. In this hollow, powder material of the order of several μm in diameter was found, and such a state continued into the nozzle hole.

Table 4. Single-cylinder engine test conditions

Symbol	Nozzle Temp. (°C)	Air/Fuel ratio	Smoke (B.S.U.)	90% Distillation Temp. of Fuel (°C)
A	165	12	0	150
B	100	12	0	150
C	154	10	1	150
D	155	15	0	150
E	165	12	0	168

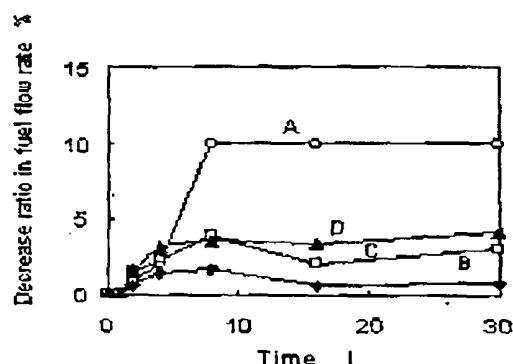


Fig. 4 Fuel flow rate change with passage of time

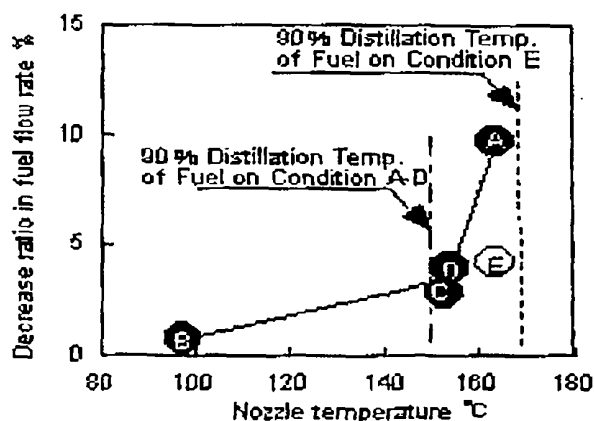


Fig. 5 Relation between nozzle temperature and decrease ratio in fuel flow rate

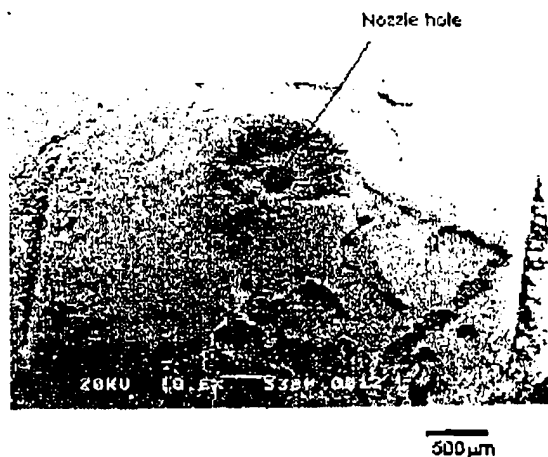


Fig. 6 Photograph of nozzle surface at 30 h

The accumulation processes of the deposits on the outside surface of the nozzle and in the nozzle hole under condition A are shown in Fig. 7, 8, 9. Figure 7 is a photograph of the nozzle before the test. The metal surfaces of the outside and the inside were finished smoothly. When the test was started, some deposits began to accumulate on the outside surface at first. In the nozzle hole, however, the accumulation of deposits was not recognized until 2 hours had passed. Figure 8 is a photograph of the nozzle after 4 hours, and the flow rate was reduced 2 %. The outside surface was already covered by the deposit layer. However, on the inside wall of the nozzle hole, a small amount of deposit began to accumulate in the exit area only. When more time passed, the

deposit layer in the hole progressed upstream. Figure 9 is the state of the deposits after 8 hours. It was recognized that a part of the deposit layer had fallen off on the outside surface. In the nozzle hole, the deposit layer already covered the whole wall. The flow rate change had reduced by 10 %.

Similar observations were found under the other conditions, and it was recognized that the reduction rate of the nozzle hole area agreed with the flow rate change.

Taking into account these observed results, the accumulation process of the deposits was considered. At first, the combustion products accumulated on the surface of the nozzle immediately after the test start. The surface around the nozzle hole became wet with fuel by the injections. Accordingly, the view of the deposit layer around the nozzle hole was different from the other area. As the deposit layer around the nozzle hole grew thick, the layer extended over the exit of the nozzle hole in excess. As a result, after a fuel injection, only a small amount of fuel remained on the exit. The fuel, which had remained in the nozzle hole, received thermal influence and changed to the deposits. Consequently, the starting point of the deposit accumulation in the nozzle hole was the exit of the nozzle hole. The deposit layer gradually progressed upstream.

The relation between the nozzle temperature and the deposit layer thickness on the nozzle surface under condition A is shown in Fig. 10. Though the deposit layer grew with time, the nozzle temperature decreased. After 30 hours, the nozzle temperature increased rapidly. The reason could be that the deposit layer on the nozzle surface fell off. When the test was restarted, the nozzle temperature began to decrease again.

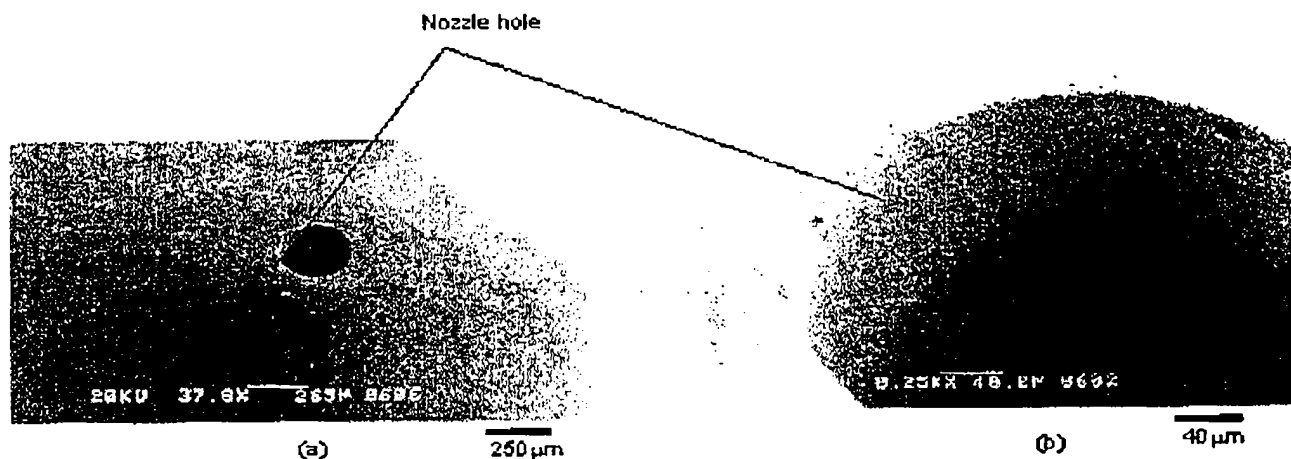


Fig.7 Photographs of nozzle surface and nozzle hole before test

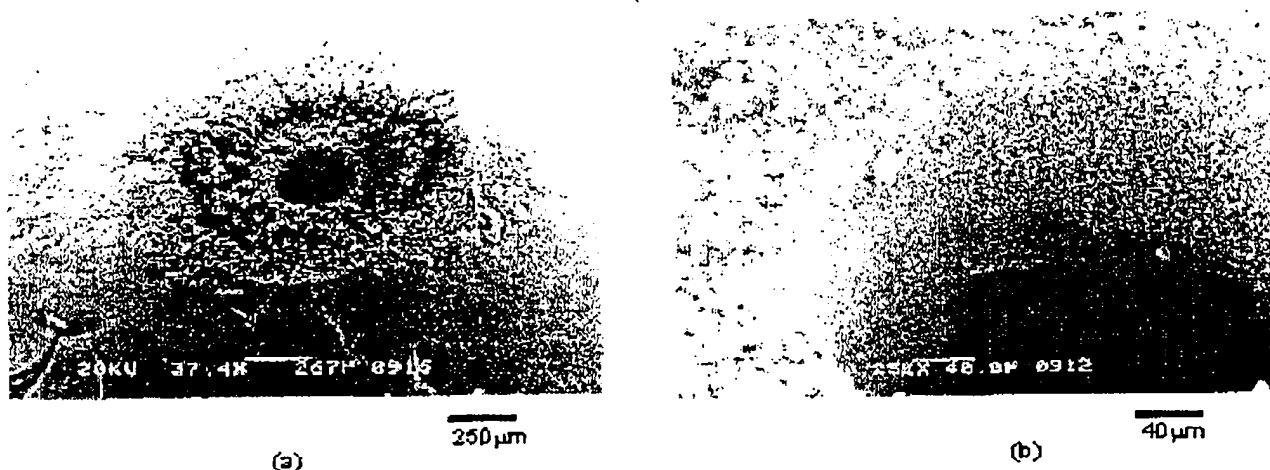


Fig.8 Photographs of nozzle surface and nozzle hole at 4 h

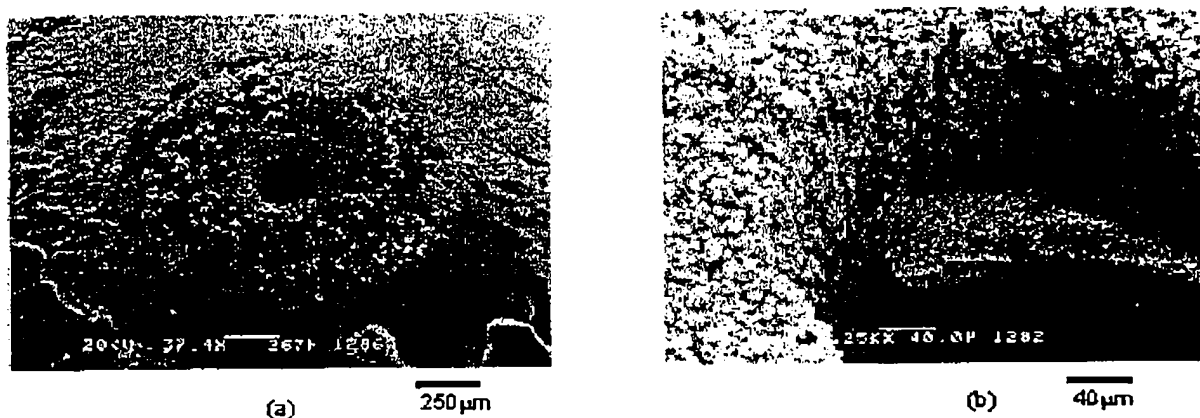


Fig.9 Photographs of nozzle surface and nozzle hole at 8 h

The reason why the decrease in the fuel flow rate continued up to around 8 hours and did not change much after 10 hours can be explained. When the engine test was started, the nozzle temperature exceeded 150°C, which was the 90 vol. % distillation temperature of the fuel. In this circumstance, the deposit formation could progress in the nozzle hole, and the flow rate changed increased rapidly. Naturally, the combustion products also accumulated on the nozzle surface under this condition. The deposit layer which accumulated on the nozzle surface acted as a heat insulator. The nozzle temperature gradually became lower because of the combustion products accumulating on the surface. As a result, the formation of the deposits in the nozzle hole was restrained after 8

hours, because the nozzle temperature was less than the 90 vol. % distillation temperature of the fuel.

Because the major ingredients of the deposits on the nozzle surface were the combustion products, strong cohesion did not exist between the deposits and the nozzle surface. As a result, when the thickness of the deposit layer became about 0.2-0.4 mm, part of the layer fell off the nozzle surface as shown in Fig. 10. On the other hand, the deposits in the nozzle hole mainly changed from the residual fuel due to thermal influence. For this reason, strong adhesion existed between the deposits and the wall of the nozzle hole. As a result, the deposit layer in the nozzle hole resisted the fluid power of the fuel injections.

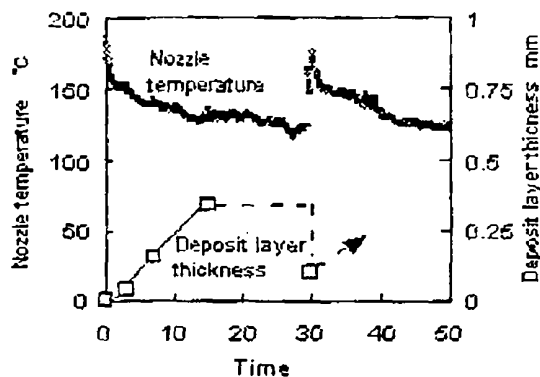


Fig. 10 Relation between nozzle temperature and deposit layer thickness on nozzle surface

DEPOSIT FORMATION MECHANISM IN NOZZLE HOLE – Taking these experimental results into account, the mechanism of the deposit formation in the nozzle hole was considered. Though it is known that dehydration reactions and heat resolution reactions generally occur in the early stage of heat resolution of the fuel, it is difficult to specify the processes in these reactions. The material becoming the nuclei in these reactions seems to be different under various conditions. This material is called "Deposit Precursors" in the reference (9).

A model of the deposit formation processes in the nozzle hole is shown in Fig. 11. After a fuel injection, a small amount of fuel remains in the nozzle hole. Deposit precursors are homogeneously dispersed in the residual fuel in the nozzle hole (Fig. 11a). As time passes, the fuel will evaporate in the nozzle hole, and cohesion of the deposit precursors will progress in the fuel. When the nozzle temperature is lower than the 90 vol. % distillation temperature of the fuel, some fuel evaporates, and some of the fuel remains in a liquid state. Thus, the deposit precursors are maintained in a state of dispersion in the fuel (Fig. 11b). In such a state, the deposit precursors are easily washed away from the nozzle hole by fuel injections. On the other hand, when the nozzle temperature is higher than the 90 vol. % distillation temperature of the fuel, most of the fuel evaporates. The deposit precursors cohere to each other, and they adhere strongly on the nozzle hole wall (Fig. 11c). These deposit precursors in this state are not easily washed away by the fuel injections, and the deposit precursors remain in the nozzle hole. As a result, the deposit formation thus progresses in the nozzle hole.

From the point of view of restraining the deposits, it is most important that the fuel that remains in the nozzle hole is always kept in a liquid state. As a result, the deposit precursors are easily washed away by fuel injections. To satisfy this requirement, it is necessary that the nozzle temperature is lower than the 90 vol. % distillation

temperature of the fuel (10), which was the most important index to suppress the deposit formation.

Though this model can qualitatively explicate the deposit formation processes in the nozzle hole, it requires further study, because it lacks a factor for the reaction rate of the deposit formation. Figures 1 and 2 showed that the deposits were formed most at 3500 rpm and the 30 mm³/st neighborhood, which was the highest temperature condition. When the engine speed is lower, there is a longer interval between the fuel injections. However, the deposit formation depends only on the nozzle temperature. If the injector had been under the 90 vol. % distillation temperature of the fuel for a long time, the deposit formation might progress. To resolve plainly the reason why the deposit formation depends only on the nozzle temperature, the reaction rate of the deposit formation must be known.

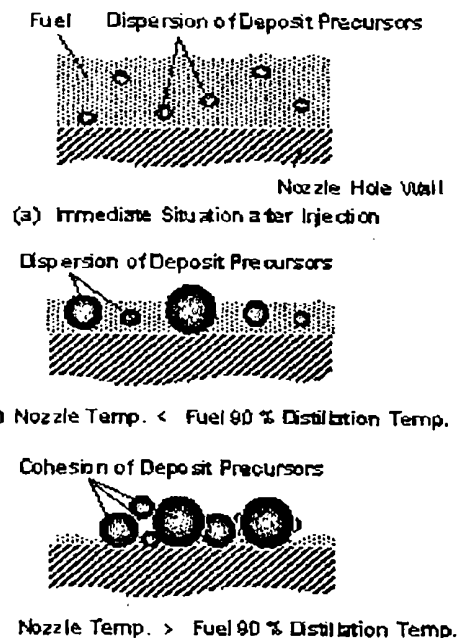


Fig.11 Model of deposit formation in nozzle hole

COUNTERMEASURES FOR SUPPRESSING DEPOSITS – Some countermeasures to keep the nozzle temperature below the 90 vol. % distillation temperature of the fuel are discussed here. There is little freedom in the installation position of the fuel injector for a direct injection gasoline engine with four valves. One effective means was to place cooling passages in the engine head in the nozzle neighborhood. Another effective means for decreasing the nozzle temperature was to place a member having a high heat conductivity rate into the space between the nozzle and the engine head. Moreover, installing a heat insulator on the part of the nozzle

surface exposed to combustion gas was also effective. Figure 12 shows calculation results, which show the nozzle temperature reduction obtained by using a heat insulator. This calculation executed a stationary thermal conductive model on the second dimension with an axial symmetry. For the nozzle and engine head which were exposed to the combustion gas, the heat transfer was set at the boundary conditions (the circumference temperature is 500°C, the heat transfer coefficient is 3.82×10^{-4} W/mm²/K). The other side of the engine head was also set on a heat transfer condition (the circumference temperature is 80°C, the heat transfer coefficient is 6.5×10^{-3} W/mm²/K). In this example the nozzle temperature without a heat insulator was 180°C. When a lower heat conductivity insulator or a thicker heat insulator was placed on the nozzle surface, a greater decrease in the nozzle temperature could be recognized.

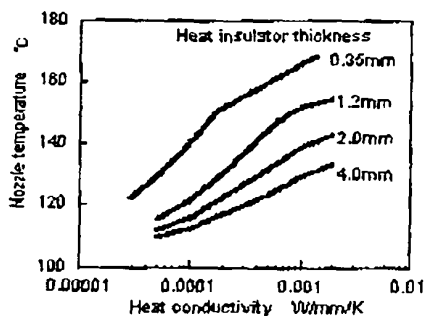


Fig.12 Effects of heat insulator on nozzle surface

CONCLUSION

This study was concerned with the phenomenon of the fuel flow rate change in the injector due to the deposit accumulation in the direct injection gasoline engine. The investigation results revealed the deposit formation mechanism and the methods to suppress the deposit formation in the nozzle hole.

The following findings are summarized:

1. The fuel flow rate in the injector was found to be noticeably decreased by deposit accumulation under the condition where the nozzle temperature was over 150°C.
2. As the combustion products became thicker on the nozzle surface, the layer of the combustion products extended over the exit of the nozzle hole in excess. As a result, a small amount of fuel easily remains on the exit after a fuel injection, and the fuel receives thermal influence and changes to the deposits.
3. When the nozzle temperature is lower than the 90 vol. % distillation temperature, deposit precursors in the fuel are easily washed away by fuel injections, because the residual fuel is kept in a liquid state and the deposit precursors disperse. On the other hand, when the nozzle temperature is higher than the 90 vol. % distillation temperature, it is hard for the deposit precursors to be washed away from the nozzle hole by fuel injections, because the deposit precursors cohere each other and adhere to the wall.
4. It is necessary to restrain the deposit formation in the nozzle hole by keeping the residual fuel in a liquid state. As a consequence, the nozzle temperature has to be kept below the 90 vol. % distillation temperature of the fuel, which is the most important index to suppress the deposit.

ACKNOWLEDGEMENTS

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Study on Combustion Chamber Deposit Formation Mechanism

-Influence of Fuel Components and Gasoline Detergents-

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Toyota Motor Corp.

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Abstract

The combustion chamber deposit (CCD) forming tendency of gasoline components and detergents were investigated with laboratory tests and engine dynamometer tests. In the dynamometer tests, the driving conditions under which fuels and detergents influence CCD formation were specified, and the effects of different gasoline components and detergent blends on CCD formation were examined. In the laboratory tests, the CCD forming process was investigated thoroughly [10].

The CCD forming tendency of aromatic compounds in gasoline were dependent not only on physical properties such as molecular weight, but also chemical structure (number or position of the alkyl substituents of aromatic molecules). As for oxygenates, engine dynamometer tests with MTBE blended gasoline yielded less CCD than the test without MTBE. The CCD forming tendency of detergents correlated with the thermal decomposition tendency of the detergent package and the concentration of the main agents.

The influence of engine oil is also discussed by quotation of the latest studies.

1. Introduction

Today, more and more countries are proposing regulations that require the use of gasoline detergents to keep intake systems clean, to improve driveability and to reduce exhaust emissions [6]. In some places which already have adopted such regulations, level of the detergent dosage in gasoline has been relatively high in order to maximize the cleaning effect of the intake system. However increased detergent

dosage has also been found to increase the formation of combustion chamber deposits (CCD) [5,14]. The formation of CCD is also known to increase with increased aromatics or heavy fraction components in gasoline. CCD in gasoline engines can cause many combustion related problems, such as CCD interference with the piston motion at top dead center (sometimes referred to as "carbon rap"), increase of tailpipe emission levels [1,2], and increase of octane number requirement [3,4]. The reduction of deposits is thus important to improving driveability and exhaust emissions. Understanding the complex chemical and physical phenomena which forms CCD is a key factor in learning how to control CCD in production engines. This study examines the mechanism of CCD formation in relation to different gasoline components and gasoline detergents, proposes possible explanations for CCD formation, and suggests the favorable trends of fuel and detergents for reducing CCD.

2. Experimental Method and Results

2.1. Preliminary test : Determination of engine dynamometer test conditions

First, the driving conditions under which fuels and detergents most greatly influence CCD formation were determined in a engine speed-torque matrix test as shown in Fig.1, using a L4, 1.8L, MPI engine (Engine A). The top surface of all tested pistons were partially flattened by machining for precise measurement of CCD thickness. Engine speed was varied from 1000rpm to 4000rpm, and load was controlled from 0 to 100% WOT. As the test additive, one of the POA additives which is relatively popular in US market was selected. And Japanese typical

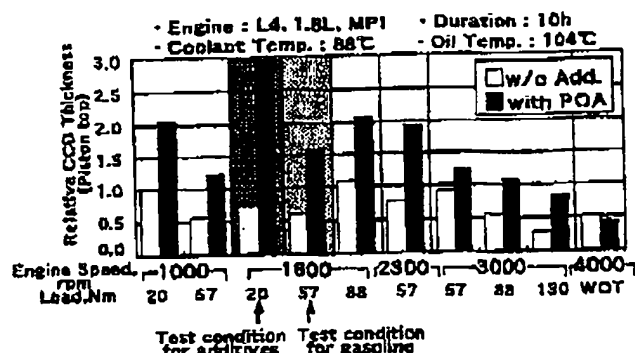


Fig.1 Effect of driving condition on CCD thickness

regular gasoline which contains 25.9 vol% of aromatics was selected as the base fuel. The main structure of CCD formed from gasoline is set within a short time and is considerably stable [7,8], therefore the duration time of all tests were decided to be 10 hours. CCD thickness was measured by the eddy-current principle at twenty five points on the piston top and fourteen points on the surface of the cylinder head. And CCD weight was measured from the difference of piston weight before and after the test. The reliability of this test procedure was ascertained in our former study using another type of engine [6], and the repeatability of both CCD weight and thickness were within 5%.

The IR peak height ratio of CCDs on piston tops are shown in Fig.2 comparing the central and the squish area. At the condition of 1600rpm x 57Nm, difference between piston top center and the squish area was the largest, which means that the contribution of gasoline concentrated in the piston top center at this condition. Thus the driving condition under which gasoline influence CCD formation the most was determined to be 1600rpm x 57Nm.

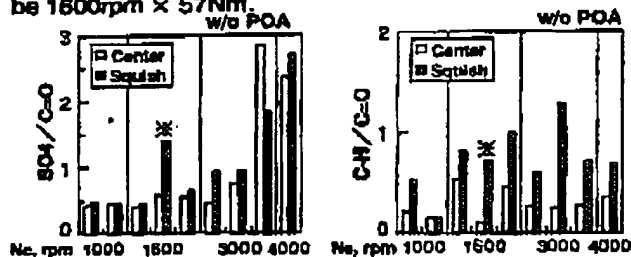


Fig.2 IR Peak height ratio of CCD on piston top

According to the test result showed in Fig.1, the difference of CCD thickness between the tests with and without detergent was the most largest at 1600rpm x 20Nm, then the driving condition under which detergents influence CCD formation the most was determined to be this condition.

Piston top temperatures were also estimated by a

hardness test at twenty five points on the piston top to identify the temperature level at each driving condition (Fig.3). The results shows that deposits were exposed to temperatures of at least 180°C [12].

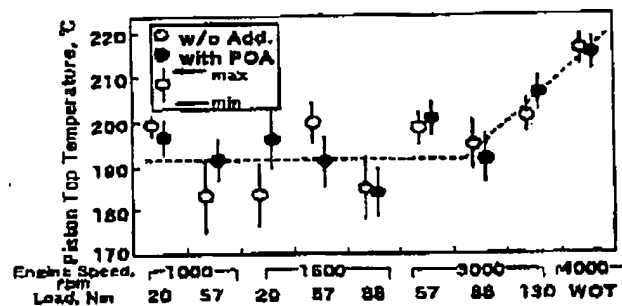


Fig.3 Estimated piston top temperature at each driving condition

2.2. Influence of fuel composition

With regard to fuel composition, we reported earlier that aromatic compounds in fuels have a strong tendency to promote formation of CCD [5]. However, we did not clarify the specific kinds of compounds that promote CCD formation [8]. Thus for this report, we made a more detailed investigation which includes both laboratory and engine dynamometer tests to help understand the process of CCD formation.

2.2.1. Engine dynamometer test

2.2.1.1. Influence of aromatic compounds

In the engine dynamometer test, we prepared specially blended fuels which consist of alkylates and pure aromatic compounds, such as toluene, p-xylene, and n-propylbenzene (Table1). The test condition is shown in Table2.

One result is that all tested aromatic compounds increased CCD amount. Another is that CCD amount did not increase directly with the change of physical properties such as molecular weights of blended pure compounds (Fig.4).

Table1 Test fuel composition

Fuel	Base	Aromatic Compounds	Blend(vol%)
No.1	Alkylate	—	100:0
No.2	Alkylate	Toluene	70:30
No.3	Alkylate	p-Xylene	70:30
No.4	Alkylate	n-Propylbenzene	70:30

Table2 Engine dynamometer test condition

Engine	L4, 1.8L, MPI (Engine A)
Engine Speed, rpm	1600
Load, Nm	57
Coolant Temp., °C	88
Oil Temp., °C	No Control
Duration, h	9
Piston top	partially flattened

Average CCD Thickness (Piston Top, μm)

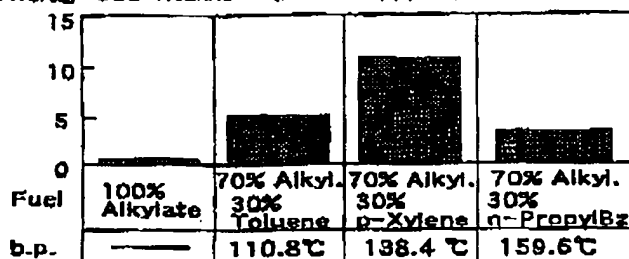


Fig.4 Effect of aromatic compounds in fuel on CCD Thickness

2.2.1.2. Influence of MTBE

As for oxygenates, effect of MTBE was also investigated by engine dynamometer test using another type of L4, 1.8L, MPI engine (Engine B). The driving condition is shown in Table3. As the base fuel, a test fuel with 98RON and 45.9% aromatics was selected (Table4). 15vol% of MTBE was blended to one fuel, the other fuel had no oxygenates. The CCD amount from the fuel with MTBE was about as half as that of the fuel without MTBE.

Table 3 Engine test condition for evaluation of the effect of MTBE

Engine	L4, 1.8L MPI (Engine B)
Engine Speed	1800 rpm
Load	39.2 Nm
Coolant Temp.	88 °C
Oil Temp.	No Control
Duration	50 (10h x 5)

Table 4 Test fuel properties

Density	g/cm ³	0.7522
Octane Number	RON	98.0
	MON	87.5
Aromatics	vol%	45.9
Olefins	vol%	18.0
Oxygenates	vol%	0.0
Dist. °C	T10	45.5
	T50	93.5
	T90	154.8

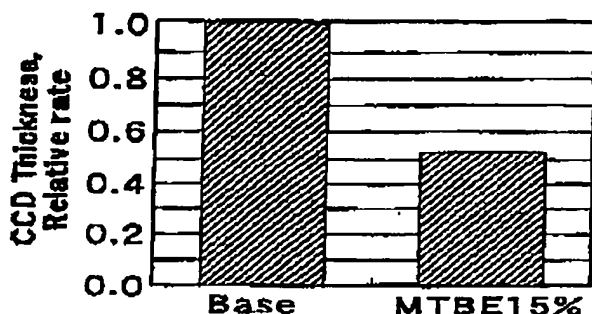


Fig.5 Effect of MTBE on CCD Thickness

2.2.2. Laboratory test

Using the results of the engine dynamometer tests, we made an investigation to find a method for measuring the CCD formation tendency of fuels without detergents or engine oil. First, we tried a "hot plate test" in the open air, at standard pressure and temperature. However, we did not find any clear relationship between fuel properties and deposit amount or deposit composition.

Under usual engine driving conditions, CCDs are exposed to temperatures of at least 180°C (Fig.3). On the other hand, the final boiling point of most gasoline samples is about 200°C, which means that deposit formation from gasoline would not proceed at standard pressure. Therefore, we used an autoclave to simulate the CCD formation tendency of gasoline at compressed atmosphere (Fig.6).

First, the CCD forming tendency of regular gasoline on the market was tested in the autoclave. The composition of the test fuel is shown in Table 5.

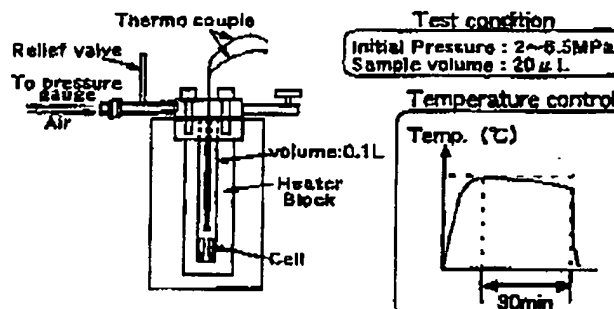


Fig.6 Laboratory test apparatus, using autoclave

Table 5 Test fuel composition

Test Fuel Composition, GC Area %	
Paraffins	48.656
Naphtens	5.812
Olefins	12.418
Aromatics	34.201
Oxygenates	0.000
Unknowns	0.916
Total	100.000

The samples are delivered in glass-cells which are set on the bottom of column. After the system is compressed to initial test pressure and sealed, the temperature is raised to the test level and then allowed to stand for 30 minutes after the temperature is reached. Next the whole column is cooled with water at room temperature. After cooling, some "autoclave-deposit" remains in the glass cells. The range of test temperature was from 150 to 300°C, and the initial pressure was varied from 2 to 6.5MPa. The most noticeable points were as follows. The weight of deposit that formed from 150°C to 220°C decreased as temperature rose; there was a peak of deposit weight

from 220°C to 300°C (at 247°C); and deposit weight went to almost zero at about 300°C. However, when we tried to form deposit in nitrogen gas (N₂) and at 247°C, deposit weight was zero, which means that the deposit formation reaction requires the process of oxidation. (Fig.7).

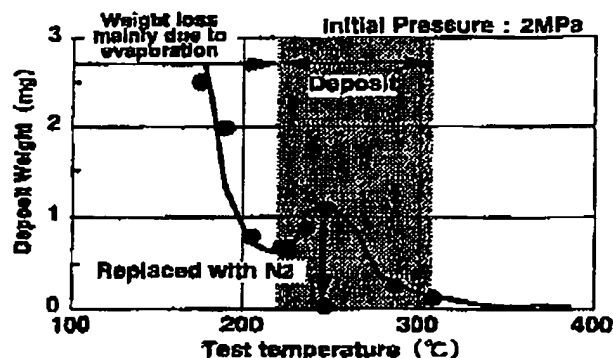


Fig.7 Deposit formation from regular gasoline in autoclave

The composition of "autoclave-deposit" was examined by infrared spectrum in comparison with CCD formed from the engine dynamometer test (L4,1.8L,MPI (Engine A), 1600rpm x 57Nm, 300h). The results are shown in Fig.8. Autoclave-deposit formed around 247°C was the most similar to CCD formed in the engine test.

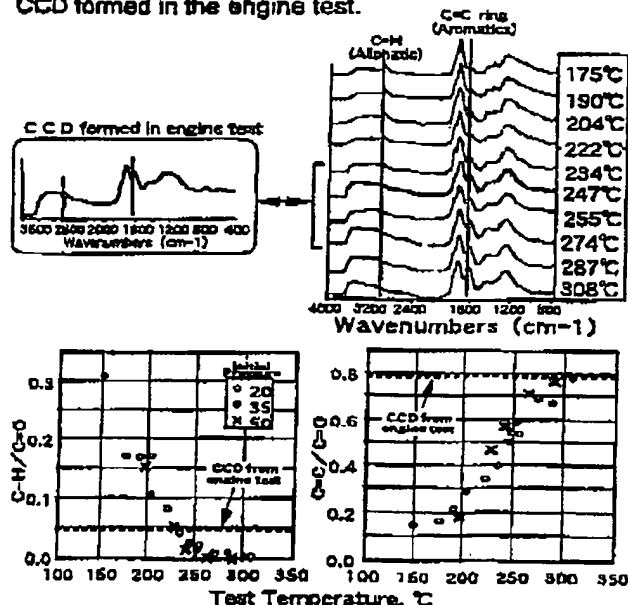


Fig.8 IR Spectra of autoclave deposit

At 247°C and 2 MPa initial pressure, which is the condition at which autoclave-deposit from regular gasoline formed the greatest amount (Fig.7), the

deposit formation tendency of pure compounds contained in typical gasoline samples were tested. The results are shown in Fig.9. The figure shows that aromatic compounds formed much more deposit than saturated or unsaturated compounds. There were also differences in autoclave-deposit amount between isomers; for example, p-xylene, m-xylene, o-xylene, and ethylbenzene. Similar tendencies were also observed between 1,3,5-, 1,2,4-, 1,2,3-trimethylbenzenes. Changes in the order of deposit amount from each of the compounds were checked at various temperatures for some of those compounds, but the order did not change with test temperature.

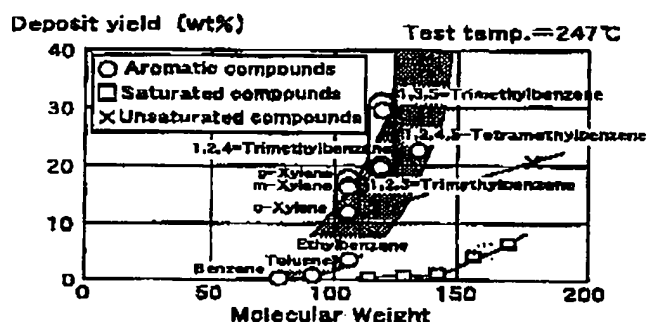


Fig.9 Amount of deposit from pure hydrocarbons in autoclave

2.3. Influence of detergents

Detergents are considered to be today's one of the main CCD promoting factors. We tested several kinds of detergents and proved that gasoline containing detergents form much more CCD than gasoline without detergents [5]. In this study we tried to find some kinds of relationships between CCD in the engine tests and laboratory tests.

2.3.1. Engine dynamometer test

First, the engine dynamometer test was performed. The test condition is shown in Table6. As the base fuel, a test fuel with properties corresponding to typical Japanese regular gasoline was selected. The properties of the fuel are shown in Table7. Four kinds of detergents that are widely used in the world market were tested (Table8). Additive B is the same as the additive which was used in the test showed in Fig.1. Dosages were 1000ppm for all detergents. For each of the tests with the four kinds of detergents, the resulting CCD amounts were much more than that of base gasoline only. However, there was no clear relationship between CCD amount and chemical type of additives (Fig.10).

Table6 Engine dynamometer test condition

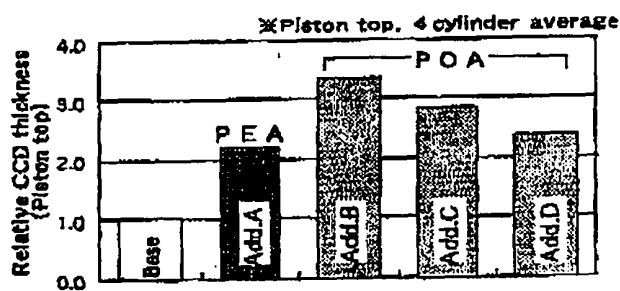
Engine	1.4 1.8L MPI (Engine A)
Engine Speed	1800
Load	19.8
Coolant Temp.	88
Oil Temp.	104
Duration	10
Piston top	partially flattened

Table7 Test fuel properties

Density	g/cm3	0.7277
Octane Number	RON	80.3
	MON	80.3
Aromatics	vol%	25.9
Olefins	vol%	18.5
Oxygenates	vol%	0.0
Sulfur	ppm	20
Dist. °C	T10	43.0
	T50	88.0
	T90	149.5

Table8 Test additive descriptions

Code	Market	Type	Dosage
A	US	PEA	1mL/1L
B	US	POA	1mL/1L
C	Japan	POA	1mL/1L
D	US, Europe	POA	1mL/1L



- Engine : L4, 1.8L, MPI
- Driving Condition : 1800rpmX20Nm
- Duration : 10h

Fig.10 Effect of gasoline detergents on CCD thickness

The chemical structure of CCD formed in the engine dynamometer test were checked by C13-NMR (Fig.11). Spectra of CCD formed from detergents added to gasoline showed the main structure of the detergents themselves. So we concluded that detergents form much greater amount of CCD because they remain in the combustion chamber in unreacted form, without being changed in their chemical structure in such condition of the test as this time.

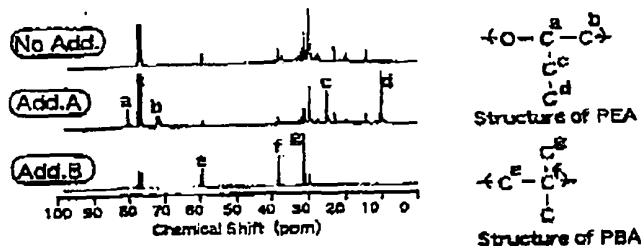


Fig.11 C13-NMR spectra of CCD

2.3.2.Laboratory test

Autoclave test results are shown in Fig.12. Autoclave-deposit forming phenomena of three kinds of additives were tested. At temperatures from 200°C to 300°C, autoclave-deposit amounts were almost constant, and then started decreasing from ca.300°C and went to zero at 400°C. Changes in chemical structure of autoclave-deposit are shown in Fig.13. Based on the above results, the contribution of chemical reaction to CCD formation from detergents should be lower than that from gasoline, and the influences of vaporization or decomposition play important roles in CCD formation from detergents.

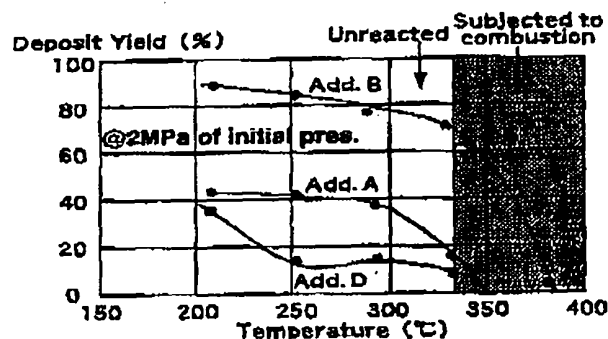


Fig.12 Weight of deposit from additives formed in autoclave

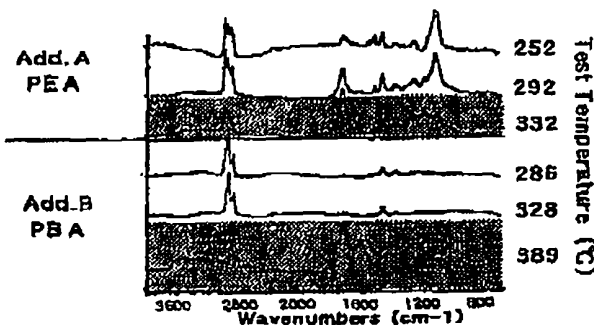


Fig.13 Change of additive's chemical structure for various temperatures

Thus, we tried TGA (Thermogravimetric Analysis) tests at standard pressure in contact with the atmospheric air. Results of the TGA analysis are shown in Fig.14. We obtained the best correlation coefficient of TGA residue and amount of the CCD described in Fig.10 at 200°C (Fig.15) [15]. Near the temperature of 200°C is where main agents in the additive package, such as surface-active agents or carrier oils, stably exist after certain kinds of solvents have vaporized (Fig.16).

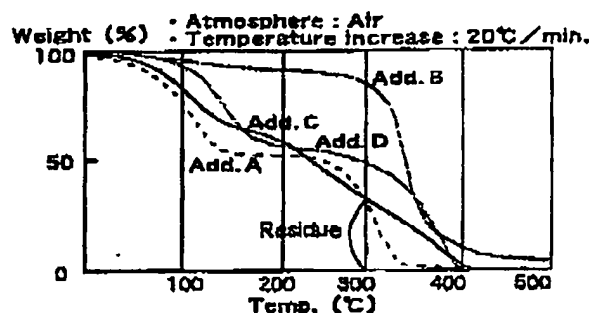


Fig.14 TGA Chart of additives

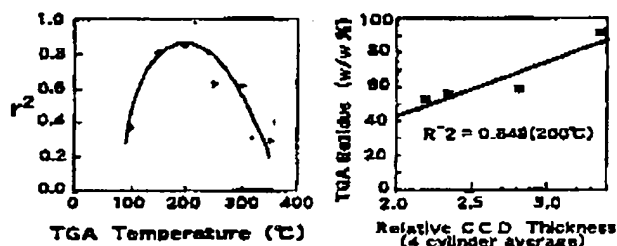


Fig.15 Relationship between CCD amount and the residue in TGA

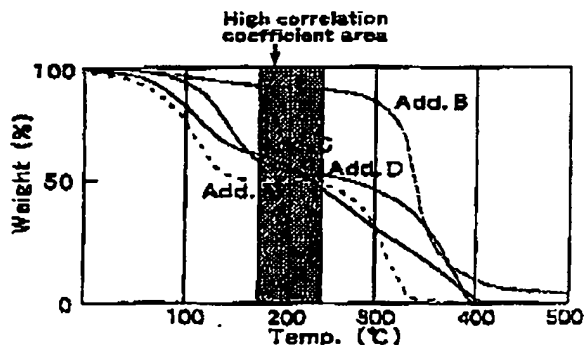


Fig.16 TGA Chart of additives (2)

3. Discussion

3.1. CCD formation mechanism

3.1.1. CCD formation from gasoline

3.1.1.1. Estimation of CCD formation mechanism

According to a study by Esaki, et al., the main

chemical units that produce CCD in the engine dynamometer test are benzene rings with a few polar groups [2,9]. This was ascertained by PGC-MS (Fig.17).

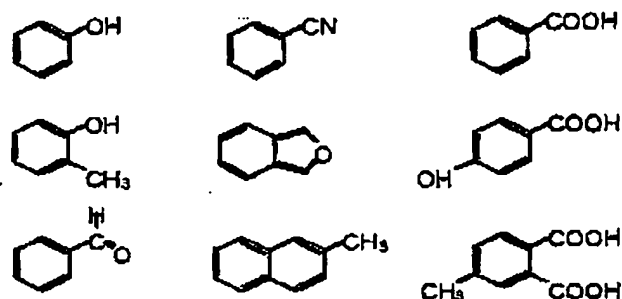


Fig.17 Chemical units of CCD
- Identified by PGC/MS -
(L4, 1.8L, MPI, 1600rpm X 67Nm, 300h)

The fact that there were no polyaromatic hydrocarbons means that the source of benzene rings of CCD from gasoline are aromatic compounds in gasoline, and the reactions in which benzene rings themselves are formed from light olefins such as acetylene are not numerous. Based on the above results, we consider that CCDs from gasoline are mainly constructed by bonding benzene rings through the mediation of polar groups.

After gasoline molecules are injected into the combustion chamber during the intake stroke, the lighter molecules are likely to evaporate, and the heavier components such as aromatic compounds are likely to collect on the surface wall of the combustion chamber or piston top in liquid phase, being adsorbed in oil films. In the compression stroke, temperature and pressure of the atmosphere rise and the hydrocarbons in oil films are oxidized somehow. And in the combustion stroke, part of the adsorbed hydrocarbons which are outside the flame, as they are already oxidized and polymerized somehow, remain in the combustion chamber to be CCD.

In short, CCD formation from gasoline, especially from aromatic compounds, requires two indispensable processes. One is oxidation, and the other is polymerization by bonding through polar groups. When the atmospheric temperature is above 200°C, deposit formation from gasoline must proceed under compressed atmosphere. If gasoline molecules are held in flame, all molecules are burned out because they are all organic compounds. So deposit formation from gasoline is considered to take place outside the flame, such as in the quench zone.

(1) Effect of the number of substituents

Alkyl substituents of aromatic compounds tend to be converted easily to carboxyl groups at high temperature and high pressure. Deposit from aromatic

compounds in gasoline is formed through the reaction between polar groups of aromatic molecules. Therefore, the fewer numbers of substituents an aromatic compounds has, the lower amount of CCD is formed.

(2) Direction of substituents

The infrared spectrum of autoclave-deposits from o-, m-, and p-xylene were checked with and without regular gasoline (Fig.18) .

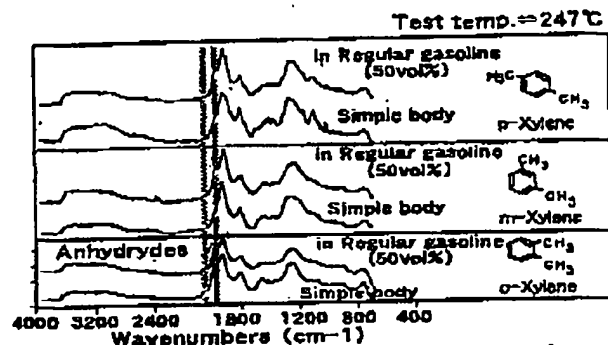


Fig.18 IR spectra of deposit formed from xylenes

Only for autoclave deposit from o-xylene did the absorption originated by anhydrides. Thinking over this point, the reason why o-xylene formed a lesser amount of autoclave deposit than m- or p-xylenes is thought to be as follows. Deposit formation reaction requires the process of oxidation of substituents of aromatic compounds, and oxidized substituents, such as carboxylic groups, function as the chain between benzene rings. However, oxidized molecules from o-xylene easily convert to anhydride, which means that molecules lose the chain of deposit formation, so m- or p-xylene form a greater amount of deposit than o-xylene (Fig.19) .

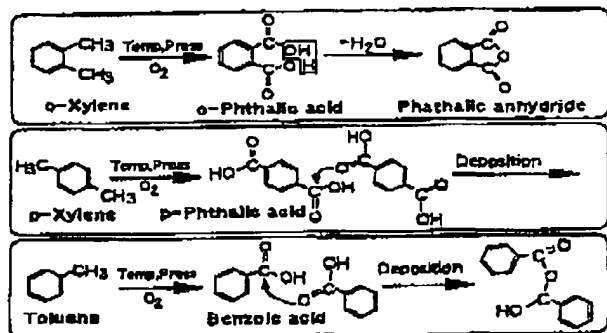


Fig.19 Estimated mechanism of deposit formation from pure aromatic compounds

3.1.1.2. Confirmation of predicted mechanism by engine test

The above-mentioned theory was affirmed by engine dynamometer tests. The test engine is the same as

used for the determination of the driving pattern, (of which pistons were partially machined) . Engine speed and load were 1600rpm x 57Nm, and the duration time was 10 hours. The results are shown in Fig. 20.

Table9 Test condition of the engine test for confirmation of the mechanism

Engine	L4.1.8L,EFI (Engine A)
Engine Speed ,rpm	1600
Load ,Nm	57
Coolant Temp. ,°C	88
Oil Temp. ,°C	104
Duration ,h	10
Piston	machined

Table10 Composition of the test fuel

Fuel	Base	Aromatic Compounds	Blend(vol%)
No.1	Alkylate	—	100:0
No.2	Alkylate	Ethylbenzene	70:30
No.3	Alkylate	p-Xylene	70:30
No.4	Alkylate	p-Xylene	70:30

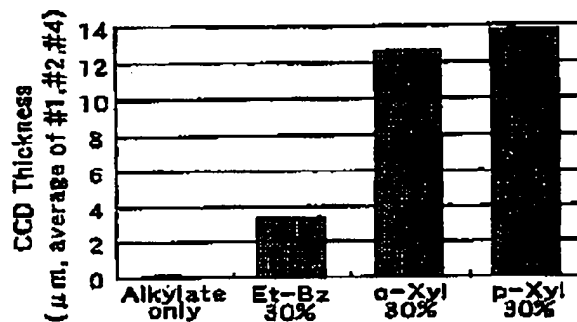


Fig.20 Effect of aromatic isomers in fuel on CCD thickness

Comparison of the test results between engine and laboratory tests is shown in Fig.21. High correlation was obtained between the result of engine tests and laboratory tests.

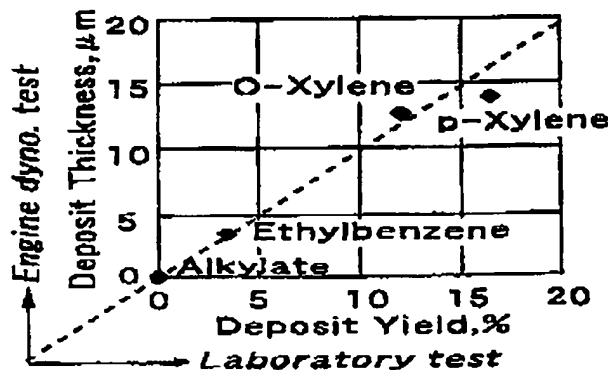


Fig.21 Relationship between engine test and laboratory test

3.1.1.5. Influence of MTBE

As for oxygenates, the CCD amount from the fuel with MTBE was about as half as that of the fuel without MTBE. Because the engine has been designed to be used with 90RON gasoline, ignition timing was to be the same for the two fuels. Considering the predicted mechanism, addition of oxygen is thought to promote the formation of CCD, however the result was opposite.

The reason is thought to be as follows. More alkyl radicals are thought to be yielded in the combustion chamber when the C-O bonds of MTBE are cut off, and they may burn off more CCD than the case of without MTBE. However it is merely a guess.

3.1.2. CCD formation from detergents

Relationship between CCD thickness and piston top temperature is shown in Fig.22. These data is of the test described in Fig.1,2 and 3. According to Fig.22, amount of the CCD formed from the fuel with detergent apparently depends on the piston top temperature in comparison with the case without detergent. After all, CCD formation from detergents is strongly influenced by the atmospheric temperature.

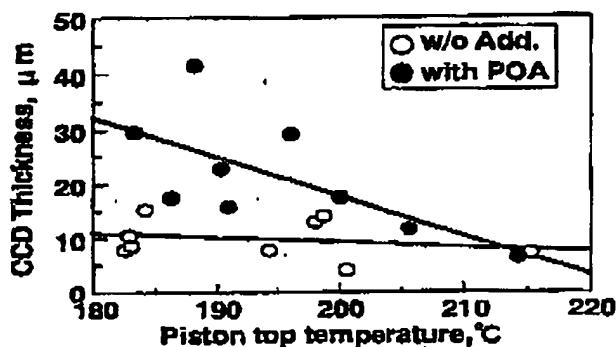


Fig.22 The temperature dependence of CCD amount

Detergents are supposed to form CCD by remaining in combustion chamber with their main agents hardly reacted. The main structure of the main agents were found by chemical analysis of CCD formed in engine dynamometer test driven at the condition under which detergents influence on CCD amount most effective. Also, the chemical structures of detergents changed quickly and dramatically with temperature rose in a narrow range in the autoclave test, with deposit weight decreasing.

So the concentration and the thermal decomposition tendency of the main agents without solvents have the greatest influence on detergents' CCD forming tendency.

3.1.3. CCD formation from engine oils

According to the study by Esaki et al., engine oil forms CCD by losing base oil by evaporation or decomposition, while partially oxidized. And when exposed to high temperature, oil additives are condensed and reacted to be inorganic compounds. However under moderate engine driving condition, contribution of engine oil, especially of oil additives is not so great (Fig. 23).

As for effects of oil blend or type of oil additive, Cheng Shi-way S have studied this topic thoroughly [16].

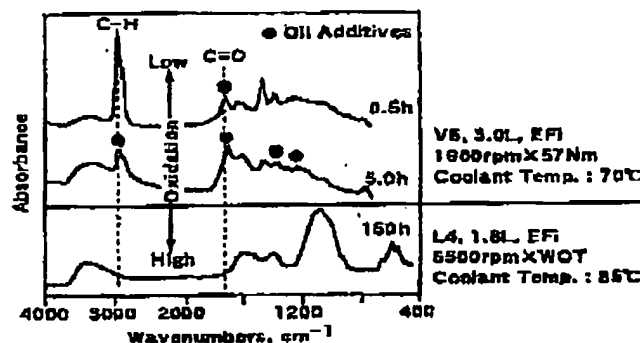


Fig.23 IR spectra of CCD formed on intake side fringe of piston top

3.2. Consideration by the observation of CCD formed in engine tests [8,11]

3.2.1. Effects of driving condition and the POA detergent

3.2.1.1. Piston top center (Appendix 2,5)

As for the CCDs formed in the test without additives, change of the color with the change of driving condition is dependent on the torque rather than the engine speed. With increase of torque, for all engine speeds, the color of the CCDs tend to turn blacklike, and some cracks appear on the CCD surface. In the case of high engine speed and high torque, as 3000rpm x 130Nm or 4000rpm x WOT, colors turn bright and marks of machining appear on the piston top surface. These marks are also found in the case of the tests driven at low engine speed and low torque.

In case of the tests with POA additive (Additive B), black grains are found on the piston top in all tests. Piston surface is found in the tests driven at low speed and low torque because the size of the grains are rather small. Checking the effect of the torque using the photo of three tests driven at 1600rpm, at 20Nm, grains on the piston top look liquid like rather than solid. However the grains look almost coagulated and some cracks are found at 57Nm. At 88Nm, cracks are propagated more finely.

In the driving condition of 1600rpm x 19.8~57Nm, 8at which the difference of CCD amount between with /

without PDA additive are the greatest, detergents don't appear to have reacted chemically.

According to the appearance of the CCDs on the piston top center (on which the effect of engine oils are thought to be less than on the squish area) large amount of CCD is formed at the conditions of low speed and low torque. However, at the range of very low speed and torque, effects of additives are not seen clearly. This is probably because of the low supply of the detergent itself at very low speed and torque.

3.2.1.2. Intake squish area (Appendix 1,4)

The most significant feature in the tests with detergents is the existence of orange colored liquid like substance found at 1000rpm and 1600rpm \times 20Nm (Appendix 4).

At 1000rpm, the deposits are almost transparent, however, there appear some black spots at 1600rpm. It is not clear that the transparency depends on either the amount of CCD or the level of chemical change. At any rate, the amount of CCD formed at 1600rpm is much more than at 1000rpm (Appendix 4).

3.2.1.3. Exhaust squish area (Appendix 3,6)

In the case of the test at 4000rpm \times WOT with detergent, the piston top is much more clear than the case of without detergent (Appendix 4). According to this observation, detergents may become effective for removal of the CCD at very high speed and very high torque.

3.2.2. Effect of the fuel components (App. 7)

All tests were performed at 1600rpm \times 57Nm. There was hardly any CCD formed from 100% alkylate fuel. In this case, the effect of fuel is very small, and there is no effect of detergents, so black spots on the intake squish area are thought to be from engine oil.

Generally, the thickness of the CCD increases with the darkness of the color. Although the difference of o-xylene and p-xylene was very apparent in the autoclave tests, the difference of the thickness of the CCDs formed in engine tests were not so large. However the average size of the grains on the squish area in the case of p-xylene is larger than that in the case of o-xylene. Although the molecular weights of three compounds are the same, the colors in the case of o-, and p-xylene are much darker than that of ethylbenzene.

3.2.3. Effect of detergent type (Appendix 8)

The most significant point is that the size of the grains varies with additive type. The common feature is that the size of the grains on the intake squish area are larger than that on the exhaust squish area at 1600rpm \times 20Nm. At the higher driving conditions, all grains are

black and seem to be carbonized more thoroughly than that formed at the lower load driving condition (1600rpm \times 20Nm.)

3.3. Total mechanism of CCD formation

Finally, the CCD formation mechanism from gasoline, detergents including engine oil are estimated as shown in Fig.24.

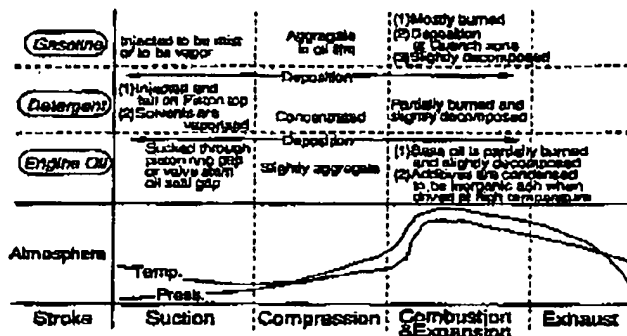


Fig.24 Estimated total mechanism of CCD formation

3.4. Suggestions for reducing CCD

3.4.1. Gasoline

Decreasing the amount of aromatics is thought to be the most effective method to reduce CCD caused by gasoline. However, aromatics play some important roles in gasoline, such as increasing octane number. If aromatics were removed and replaced by alkylate to maintain octane number, then gasoline refining cost would rise dramatically. Using 100% alkylate gasoline might cause some problems with startability. The use of aromatics with fewer substituents or o-compounds is the desirable trend for gasoline composition in order to decrease CCD amount caused by gasoline.

3.4.2. Detergents

There are two desirable trends for detergents. One is that the dosage of main agents must be decreased as much as possible, and the other is that main agents must be easily decomposed with temperature. However, detergents which are easily decomposed are said to have less ability to clean up the intake system, so compatibility of the two features is important.

4.C nclusion

4.1.CCD formation from gasoline

- (1) Gasoline forms CCD under compressed atmosphere and outside the flame in the quench zone.
- (2) Some types of substituents are oxidized, and they play a role for binding heavy groups such as benzene rings. From this point of view, aromatics are likely to provide a core for the CCD formation process because of the stability of benzene rings.
- (3) Aromatic compounds with lower numbers of substituents, or with substituents that are located side by side, such as o-compounds are favorable for reducing CCD caused by gasoline.

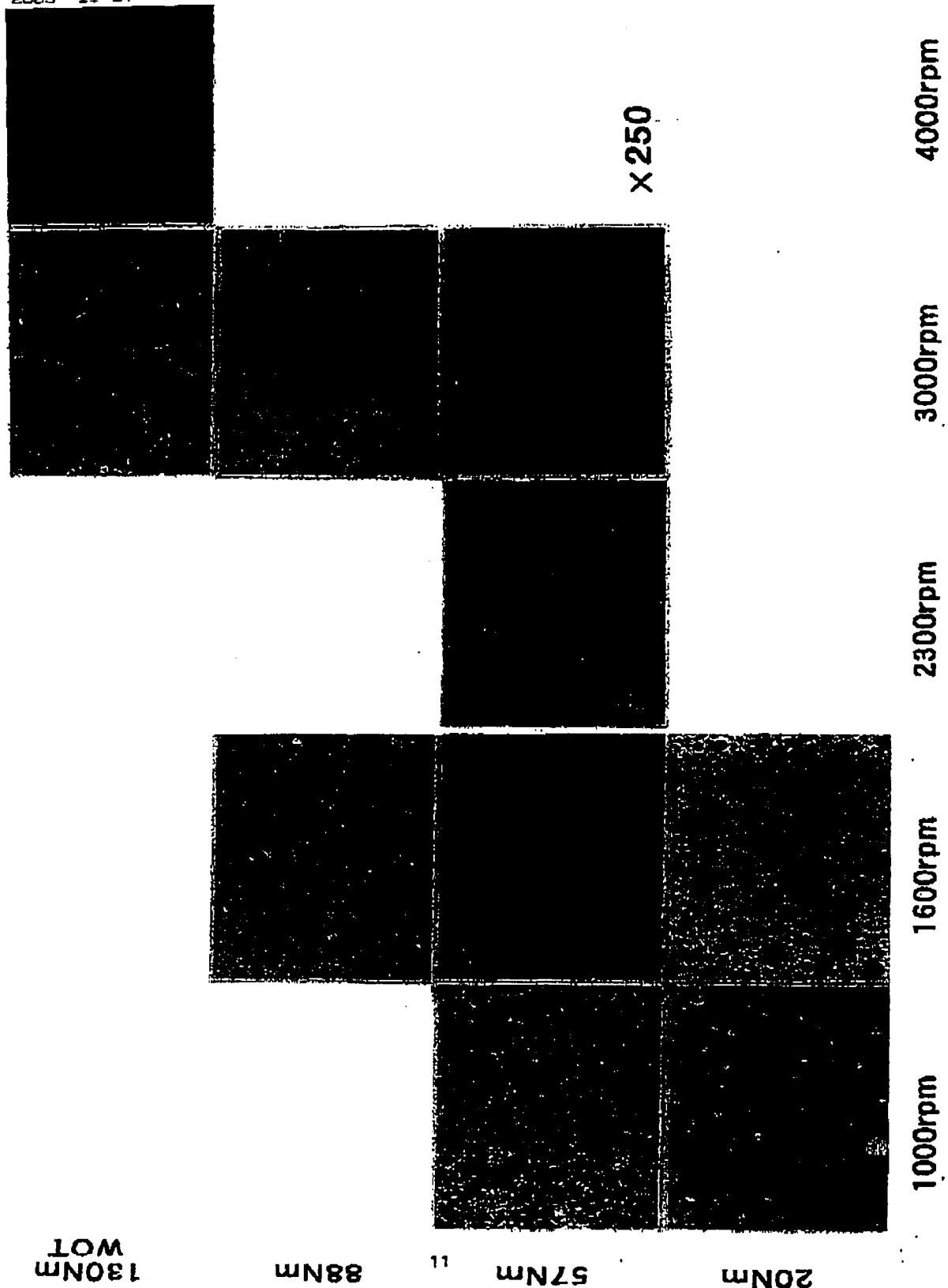
4.2.CCD formation from detergents

- (4) Detergents form CCD by remaining in the combustion chamber almost without chemically reacting.
Decreasing the amount of main agents is effective for reducing CCD. However there must be enough detergent to maintain or clean intake system.
- (5) Properties such as ability to be decomposed or to be pyrolyzed are favorable for reducing CCD.

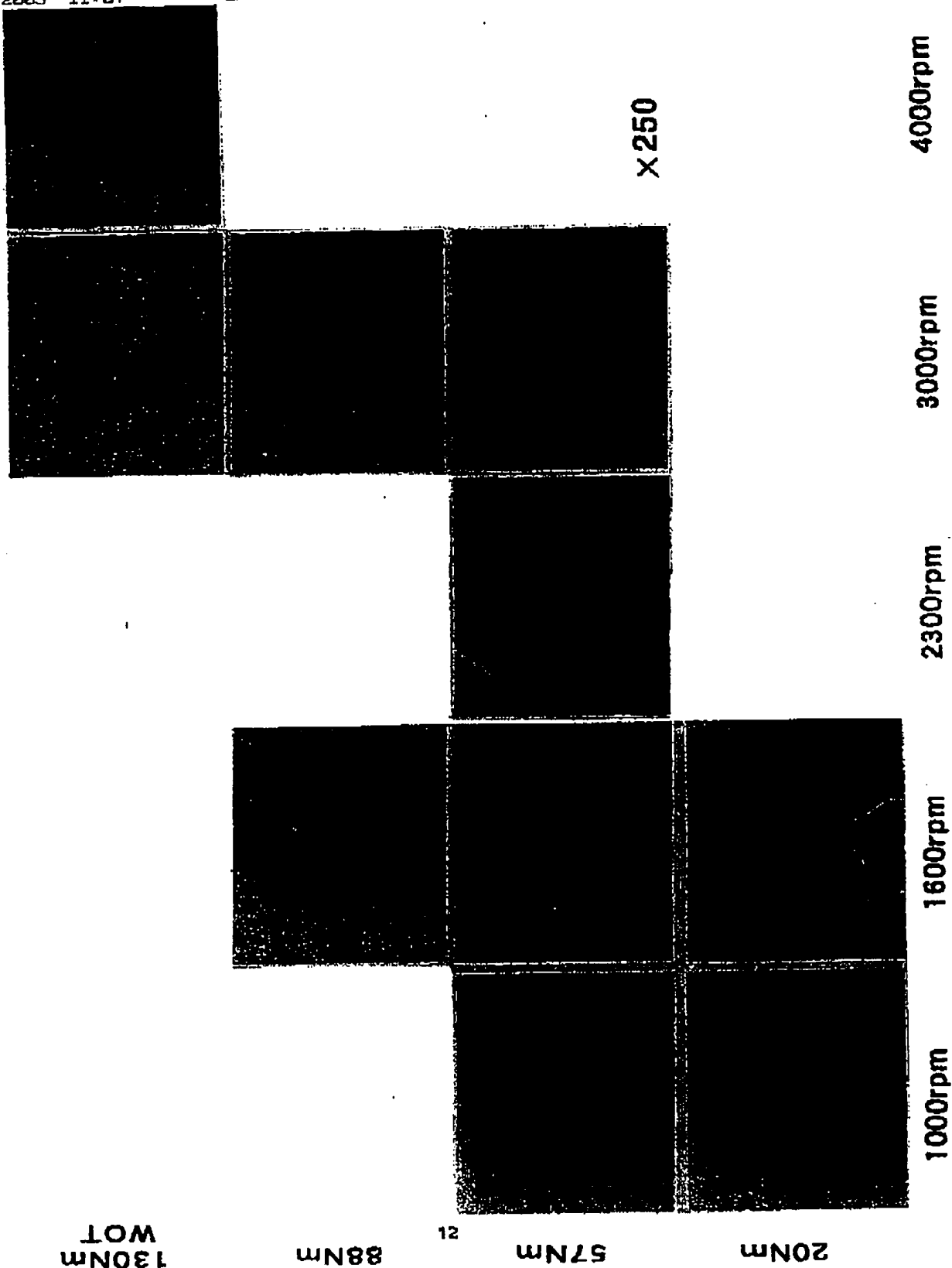
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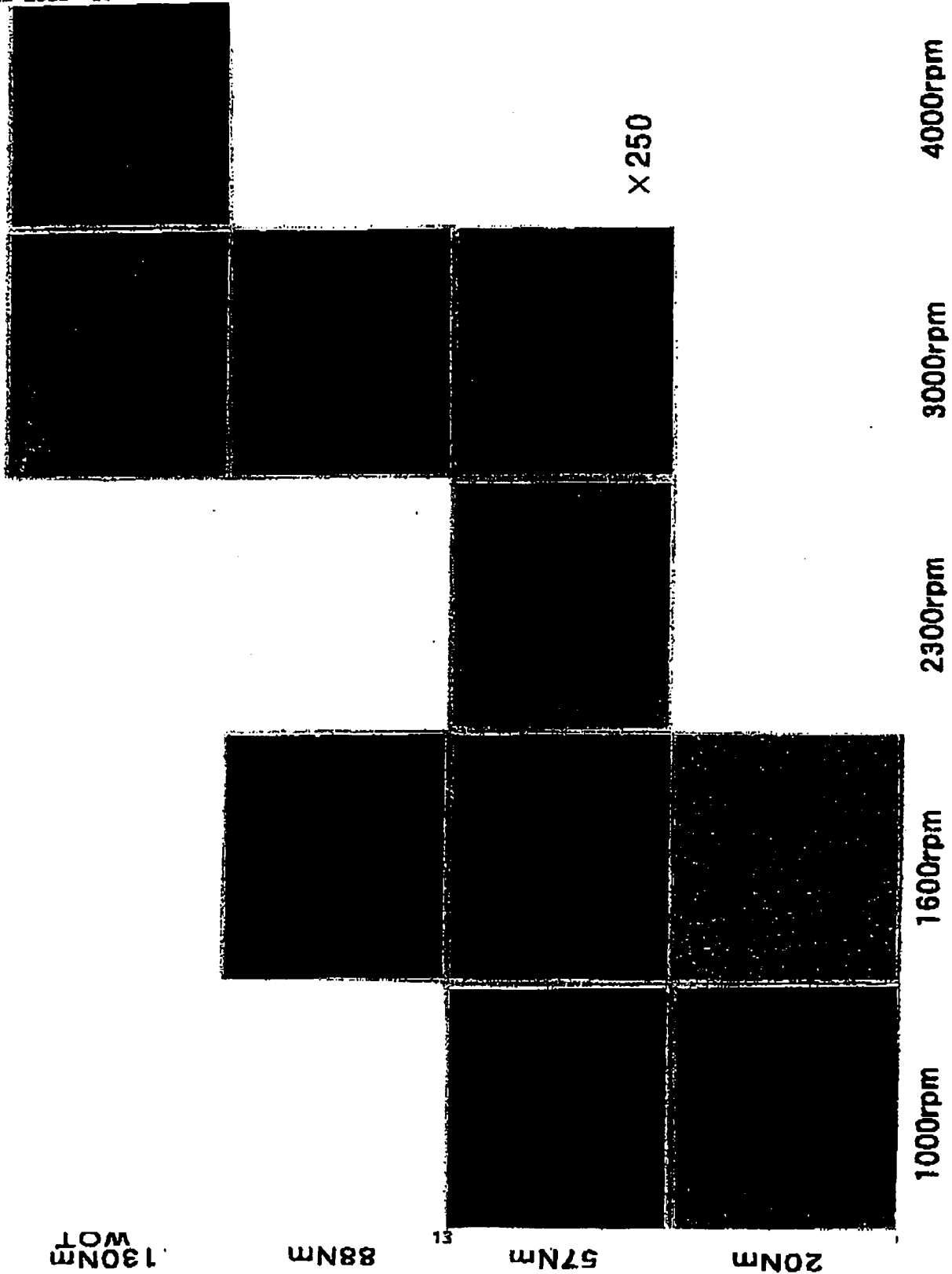
Appendix 1. Matrix test - No additive, Intake squish area



Appendix 2. Matrix test - No additive, Piston top center



Appendix 3. Matrix test - No additive, Exhaust squish area



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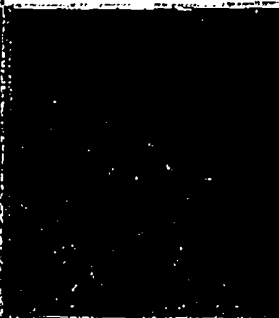
Appendix 4. Matrix test - POA added, Intake squish area

Additive B



X 250

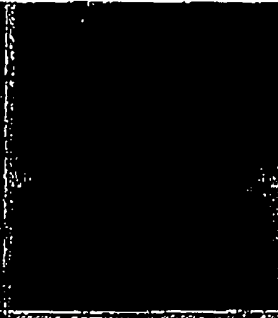
4000rpm



3000rpm



2300rpm



1600rpm



1000rpm

130Nm
WOT

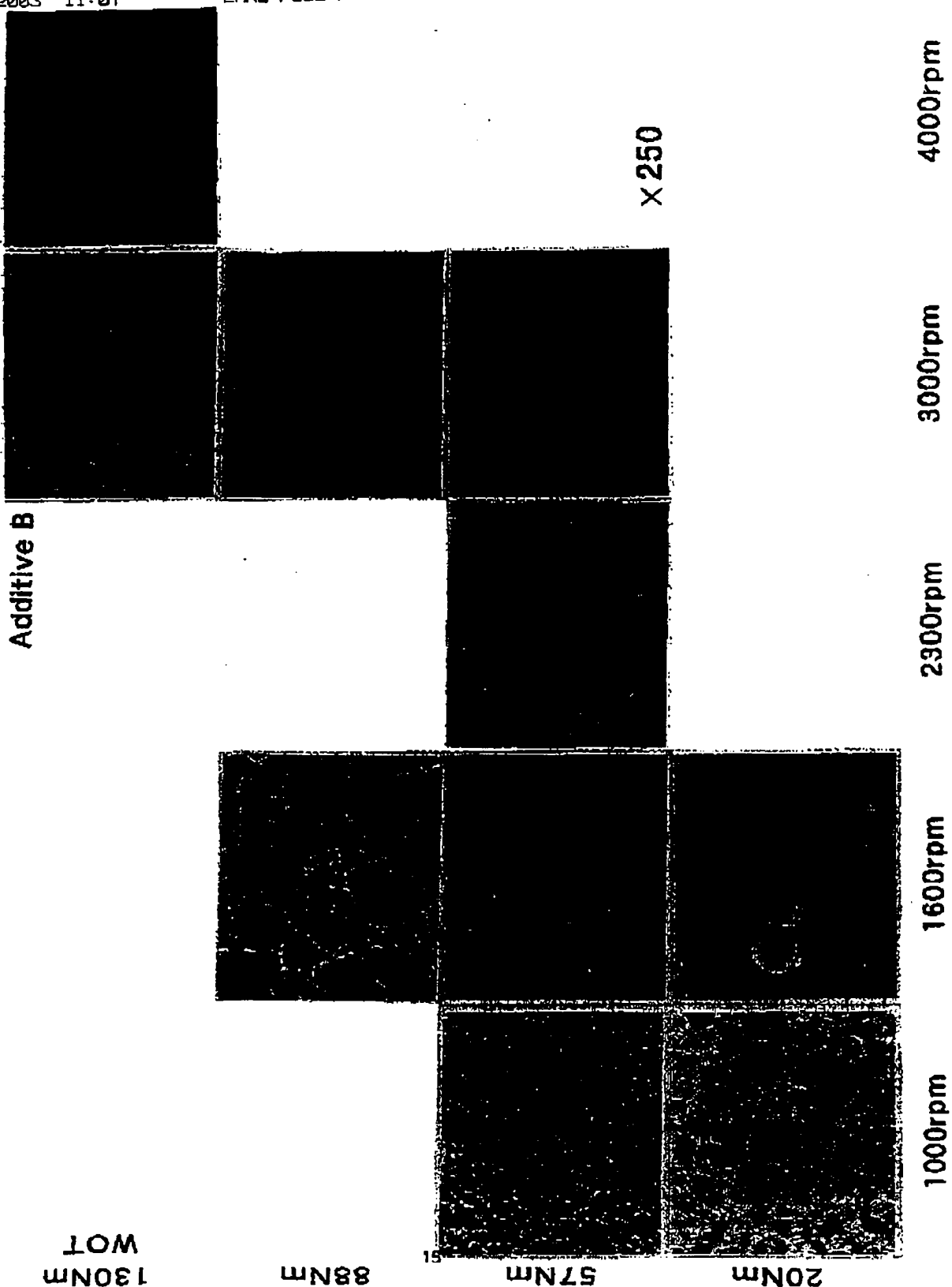
88Nm

14

57Nm

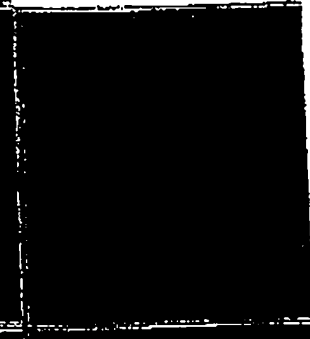
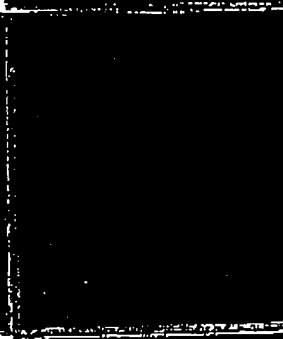
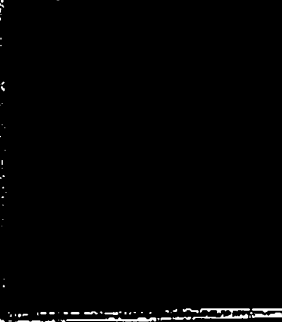
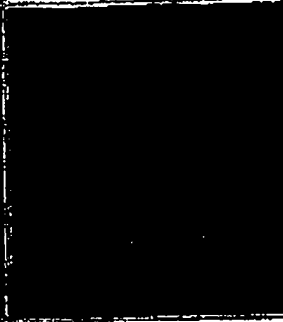
20Nm

Appendix 5. Matrix test - POA added, Piston top center



Appendix 6. Matrix test - POA added, Exhaust squish area

Additive B



X 250

4000rpm

3000rpm

2300rpm

1600rpm

1000rpm

130NM
WOT

88NM

16

57NM

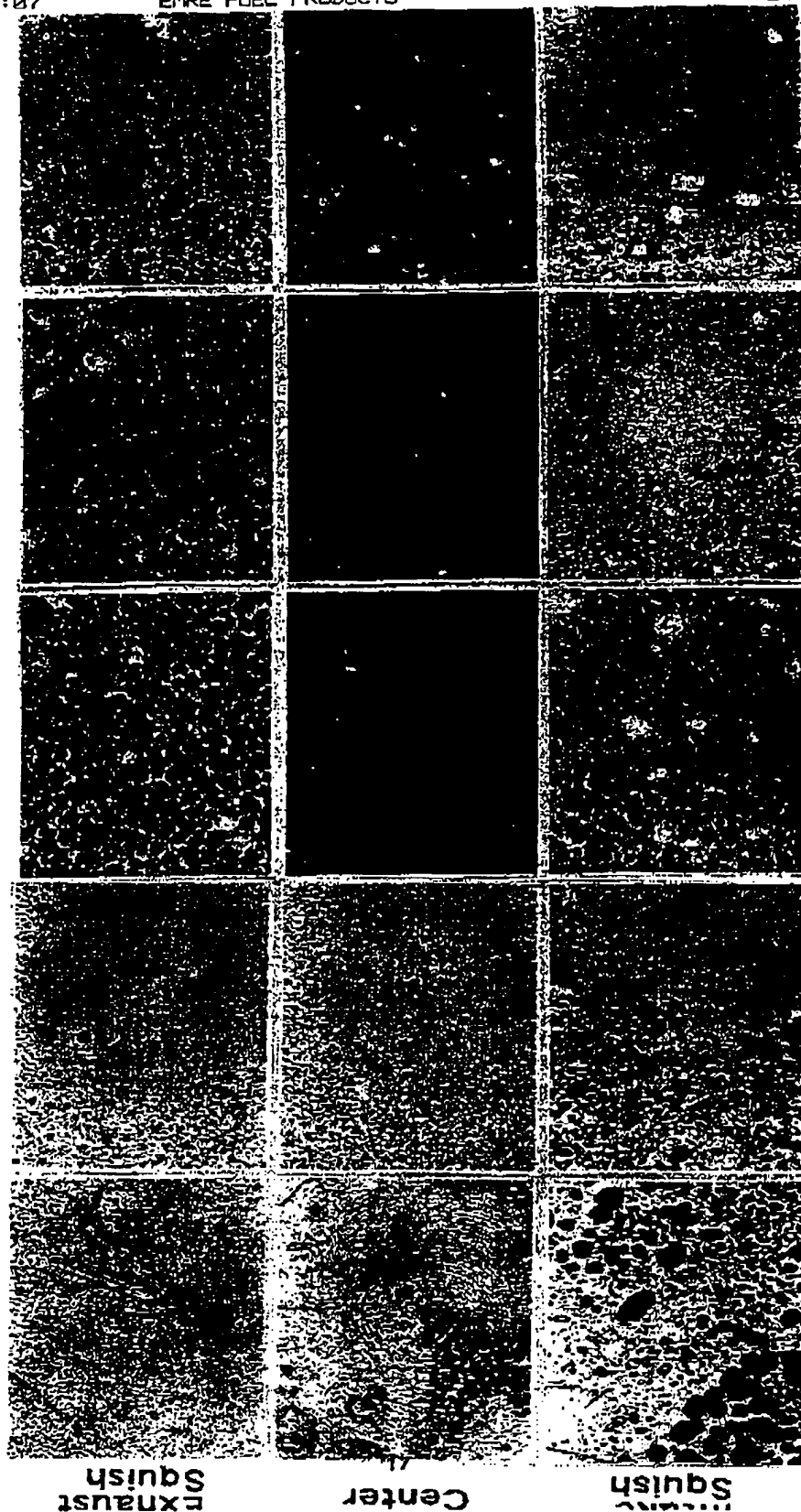
20NM

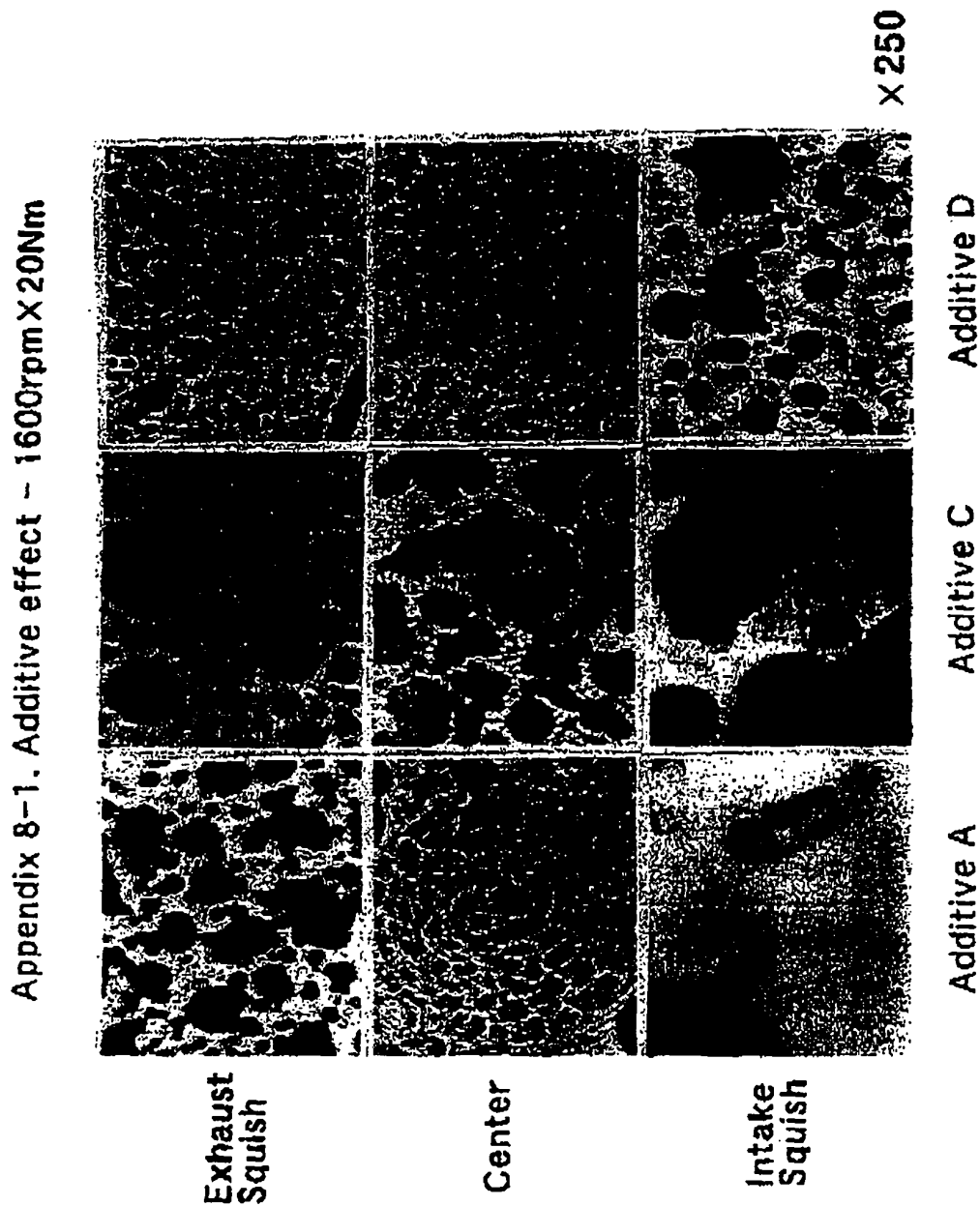
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Appendix 7. Effect of fuel component

X 250





Appendix 8-2. Additive effect - 3000rpm X 57Nm

